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LABORATORY TECHNIQUE

in

ORGANIC CHEMISTRY

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LOUIS P. HAMMETT, PH.D., *Consulting Editor*

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Laboratory Technique

in

Organic Chemistry

by AVERY ADRIAN MORTON
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First Edition

EIGHTH IMPRESSION

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PREFACE

The purpose of this book is to improve the student's understanding of ordinary laboratory manipulations and to widen the research worker's knowledge of the apparatus at his command. To fulfill properly this objective requires a detailed treatment of theory and practice not found in present-day manuals. Nor do the larger reference volumes contain a hint of the great advances that have been made in this field in recent years. This small volume, by no means intended as a bibliographical survey, seeks to present in convenient and compact form the fundamentals of the various common laboratory operations. The material included has accompanied the work in the advanced organic laboratory course at the Massachusetts Institute of Technology for many years. The author has therefore had ample opportunity to observe that the training is of practical benefit to men in research.

The author is deeply indebted to his colleagues, Professors Ernest H. Huntress, Avery A. Ashdown, Tenney L. Davis, Robert C. Hockett, Nicholas A. Milas, and Clifford B. Purves for their encouragement and support as well as for supply of materials for experiments. He is also grateful to Doctors George Thomson and Robert T. Armstrong and to the many students who have given valuable suggestions in assembly and use of apparatus. In particular is he grateful to Professor James F. Norris for his friendly criticism and comments, both in the conduct of the laboratory and in the preparation of this manual.

AVERY A. MORTON.

CAMBRIDGE, MASS.,
November, 1937.

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NOTES ON INSTRUCTION

The physical setup necessary for proper instruction will vary with the extent of the work. The author has found it advantageous to have permanent installations. Thus in the special apparatus laboratory, occupying a space approximately 18 by 12 feet, there are located six fractionating columns with connections for vacuum fractionation including automatic pressure regulators and mercury condensation pumps, a superheated steam distillation apparatus, molecular stills, eight or more continuous extraction units, a drying oven, a vacuum drier, and an Abderhalden drying tube. The usual ring stands are replaced by lengths of iron pipe extending from the desk top to a point near the ceiling and fastened rigidly to wall and desk. The additional height permits a vertical arrangement in assembling each unit with resulting economy of space. Another laboratory of equal size is devoted to physical and chemical measurements. It contains standard solutions, thermostats, a refractometer, melting-point apparatus of various kinds, and an assortment of pieces for determining molecular weights. A small laboratory contains the necessary equipment for micromanipulation. Another small room provides space for a 30-foot still. All this apparatus serves the dual purpose of providing facilities for instruction and furnishing research workers with adequate tools without loss of time in assembly.

Experiments are chosen with the idea of giving a wide variety of experience. On one hand, the student is trained in micromanipulation so that he can fractionate 20 milligrams of liquid into fifteen or twenty parts and plot the resulting curve or can carry out complete syntheses with 2 to 3 milligrams of material and obtain the correct melting point after repeated crystallizations. On the other hand, he is instructed in large-scale operations; shown how to economize by substituting digestion for crystallization, how to effect crystallization with a minimum quantity of solvent, how to filter conveniently large batches of

material. His attention is directed to the revolutionary changes that have occurred in fractionation within recent years. He is shown that the excellence of any packed column is expressed in terms of the number of theoretical plates rather than in mere height. He is introduced to vacuum technique and to molecular stills, is made acquainted with all types of distillation, and is instructed in the methods of filtration, decoloration, and chromatographic adsorption. Judgments on purity arrived at from mixed melting points and by cooling curves are studied. The excellent method of Halford in showing identity of two compounds is tested. Binary and ternary boiling mixtures receive due consideration. Physical measurements such as molecular-weight determination are not considered as being a formal part of the work. A large part of the work can, of course, be used to supplement the regular work of the ordinary advanced laboratory course.

As far as possible the work in the course is made to fit into the general research program of the department. Products of the synthetical work of research students are often taken as the material for distillation or purification. Needed preparations are made on a large scale, followed by comparison tests of different methods of purification. Compounds that have proved difficult to crystallize are put through a series of tests which are known to have been helpful in other cases, emphasis being placed on the scientific aspects of this interesting phenomenon. Large operations are reduced to micro proportions. Tarry wastes are treated in order to recover all products.

One hour a week for one term is devoted to lectures on the theory related to the operations described. Such careful study of the laboratory art has been found to be exceedingly helpful in promoting intelligent work.

NOTE: The abbreviations used by *Chemical Abstracts* are used in this text. An additional abbreviation, *Syn. Org. Chem.*, is used to stand for *Synthetic Organic Chemistry*, published by the Eastman Kodak Company.

LABORATORY TECHNIQUE IN ORGANIC CHEMISTRY

CHAPTER I

DRYING AND DRYING AGENTS

1. Apart from the drying of substances as a preliminary step to their analysis, several reasons may be cited for removing moisture. Crystallizations of hygroscopic substances are often impeded when slightly wet. Many alcohols form constant-boiling mixtures with water. Well-known catalytic effects can be attributed to minute amounts of moisture. Hydrolysis of chlorides or other organic compounds occurs when distillation is not preceded by thorough drying. For these reasons it has become common practice to dry all products. Choice of a drying agent is of utmost importance for the sake of effectiveness as well as economy of time. It would appear ludicrous to dry a gas by initial scrubbing with sulfuric acid followed by passing it through the less effective calcium chloride. Yet such errors have been reported in formal publications. Knowledge of the principles that govern this manipulation will avoid such obvious mistakes and make it possible in many cases to speed up isolation of the compound in a dry state.

2. **Classes of Drying Agents.**—Methods of drying may be classified broadly as being chemical or physical. As chemical agents we include salts that form hydrates such as calcium chloride or sodium sulfate; oxides, including either calcium oxide or phosphoric anhydride; bases or acids such as caustic alkali or sulfuric acid; and metals, as illustrated by sodium, calcium, or aluminum. By physical methods, we mean to designate such processes as fractionation, distillation of binary or ternary mixtures, application of heat or cold, adsorption, absorption, or

extraction. These agents may be used separately or together, but for our purpose it is more convenient to discuss them singly.

CHEMICAL AGENTS

3. Hydrate Forming Salts.—Under this heading we include such substances as calcium chloride, calcium bromide, copper sulfate, sodium sulfate, magnesium perchlorate, potassium carbonate, or calcium sulfate. Their efficiency obviously depends upon the vapor pressure of water above the salt. Effectiveness would be greatest at low temperatures as shown by the data¹ on calcium bromide in Table 1.

TABLE 1.—EFFECT OF TEMPERATURE ON DRYING EFFICIENCY OF CALCIUM BROMIDE

Temperature, °C.	Milligrams of water per liter of air
25	0.14
-21	0.019
-72	0.012

At higher heat levels the usefulness is considerably impaired, a fact better appreciated by examining Table 2 for the vapor pressure² of water above some salt hydrates.

TABLE 2.—VAPOR PRESSURE OF WATER OVER HYDRATES OF CALCIUM CHLORIDE

Temp., °C.	Pressure, mm. Hg	Solid phases
-55.0	00.00	Ice—CaCl ₂ ·6H ₂ O
+29.2	5.67	CaCl ₂ ·6H ₂ O—βCaCl ₂ ·4H ₂ O
29.8	6.80	CaCl ₂ ·6H ₂ O—αCaCl ₂ ·4H ₂ O
38.4	7.88	βCaCl ₂ ·4H ₂ O—CaCl ₂ ·2H ₂ O
45.3	11.77	αCaCl ₂ ·4H ₂ O—CaCl ₂ ·2H ₂ O
175.5	842.00	CaCl ₂ ·2H ₂ O—CaCl ₂ ·H ₂ O

Consequently the frequent practice of distilling a liquid over a drying salt is to be deplored if the boiling point is very high. A possible exception may exist in the case of powerful desiccants over which the vapor pressure of water is very low. Yet even

¹ Superior numerals refer to numbered items in the references given at the end of the chapter.

in these instances the agent cannot be so efficient as at low temperatures. With some salts such a practice might indeed lead to a dehydration of the drying agent itself in the same way that oxalic acid (see Table 7 for comparative vapor pressure of water over oxalic acid, sodium sulfate, and phosphorus pentoxide) is made anhydrous³ by distillation of carbon tetrachloride. Serious difficulty can be remedied by distilling under reduced pressure or by filtering prior to distillation.

4. Of all salts, *magnesium perchlorate*⁴ is the best from the standpoint of near absolute dryness. It is almost as effective as phosphorus pentoxide for drying air and has a capacity for water per unit weight several times greater than the latter. It is obtained conveniently by heating the trihydrate $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ slowly in a vacuum of less than 0.1 mm. to 250°C. This method⁵ avoids fusion of the salt at its melting point 145° and leaves the product sufficiently porous for direct use. The anhydrous commercial product is known as "Anhydron," and that with three molecules of water is called "Dehydrite." This trihydrate,⁶ at 0° and a rate of flow of air equal to 5 l. per hour, is as effective as phosphorus pentoxide; but at higher velocities, such as 10 l. per hour, the efficiency falls off rapidly. Both substances are suitable for a large number of drying operations in the laboratory and particularly for drying gases. Pumice⁷ may be impregnated with the salt to lessen the cost. Although binding of water is done through a coordinated valence and not by the normal linking, it is interesting to note that removal of water is nearly as thorough as with phosphoric oxide. This statement is given greater weight by the fact that the molal heat of hydration of magnesium perchlorate is 38,370 cal. as compared with 32,400 cal. for phosphorus pentoxide. Its great efficiency is attributed⁸ to a tendency to equalize the volumes of cation and anion by union with water, a view supported by Smeets⁹ finding that heats of hydration of perchlorates decreased as cation volumes increased. The solubility¹⁰ in water is 0.3294 gram-molecular weights per 100 ml.; in alcohols and esters it is less; and in ether is slight. Obviously, discrimination must be exercised if it is to act as a specific agent for water removal, and its use in contact with organic compounds is not without hazard (see Sec. 6).

5. *Barium perchlorate*, $\text{Ba}(\text{ClO}_4)_2$, has also been found¹¹ to be an excellent drying agent. Although it is not so good as the magnesium salt, it is better than concentrated sulfuric acid. Among the special advantages that it possesses is the ease of regeneration, for it does not fuse in its own water of crystallization during dehydration. Neither does it deliquesce in moist air beyond the trihydrate stage nor decompose on long heating at 400°C . In order to increase its efficiency, capacity, and speed yet retain its superior properties of nonfusibility and stability to heat, it may be mixed with some of the magnesium salt. Barium perchlorate is known commercially as "Desicchlora."

6. A word of *caution* needs to be inserted regarding the use of perchlorates in contact with organic solvents. Druce¹² reports that magnesium perchlorate can give rise to explosions when incautiously heated with organic solvents. This fact is a serious deterrent to its use in drying compounds dissolved in a solvent. Accidents¹³ may also happen from a chance mixture of sulfuric acid with a perchlorate, thus liberating free perchloric acid which, in contact with organic matter, produces an explosion. Spent perchlorate salts should never be thrown in waste jars or sinks but should be dissolved in water and disposed of in a drain or ditch.

7. One of the very common salts in the laboratory is *calcium chloride*, CaCl_2 . Because of its familiar use as a desiccant in the analytical laboratory the organic chemist is apt to apply it to the drying of compounds in solution. In reality its value is greatly limited by the pronounced tendency that it has of forming addition compounds with a wide variety of substances. With acetone,¹⁴ products of the composition $\text{CaCl}_2 \cdot (\text{CH}_3)_2\text{CO}$ and $\text{CaCl}_2 \cdot 2(\text{CH}_3)_2\text{CO}$ result. The addition compounds with methanol, ethanol, propanol, and butanol have long been known, and their vapor pressures¹⁵ measured. With acetamide,¹⁶ the compound $\text{CaCl}_2 \cdot 4\text{CH}_3\text{C}(\text{O})\text{NH}_2$ occurs. Glycerol¹⁷ has been recorded as yielding the compound $\text{CaCl}_2 \cdot 3\text{C}_3\text{H}_5(\text{OH})_3$. Mention might also be made of the addition compounds with gulose and mannose.¹⁸ Amines,¹⁹ *e.g.*, methylamine, $\text{CaCl}_2 \cdot 2\text{CH}_3\text{NH}_2$, and amino acids,²⁰ both alpha and beta, form complexes with calcium chloride. Diethyl succinate²¹ and ethyl diazoacetate²⁷ are known to form addition compounds with

this salt. More complete lists are given by Pfeiffer²² and by Greenbaum.²³ The collection is extensive enough, however, to suggest that the use of calcium chloride with oxygenated compounds and with substances having an NH_2 group is attended with the probability that the agent for removal of water may be even more effective for removal of the organic product.

8. *Other halogen salts* used as drying agents are magnesium chloride, MgCl_2 , and calcium bromide, CaBr_2 . The former²⁴ is claimed to be a more powerful absorbent of moisture from a current of air than is calcium chloride. The latter¹ is advantageous for drying hydrogen bromide, although it is probably no better than, if as good as, aluminum bromide if results²⁵ with the chloride in drying hydrogen chloride are a criterion.

9. *Calcium sulfate* is a recent addition to the list of commercial laboratory reagents. It is sold under the name of "Drierite." As an agent for drying air it is almost as effective as sulfuric acid. Excellence of its action for other purposes may be judged from Table 3²⁶ in which the densities of compounds, dried by distillation from anhydrous calcium sulfate, are compared with accepted values. Although direct distillation of a liquid from a drying agent subjects the desiccant to the disadvantage of having to function at a temperature higher than that at which it would be most efficient, the results are suggestive of the great possibilities of this material. Calcium sulfate has the single disadvantage of taking up only 6.6 per cent of water per weight of calcium sulfate used. There is a record of an addition compound²⁷ between two molecules of calcium sulfate and one of ethyl diazoacetate, but with the majority of organic compounds there is little tendency in that direction.

TABLE 3.—DENSITIES OF SOLVENTS DISTILLED OVER CALCIUM SULFATE

Compound	Density found	Accepted value
Ethanol.....	0.7851	0.78506
Methanol.....	0.7891	0.7898
Ethyl ether.....	0.7138	0.71352
Acetone.....	0.7842	0.7844
Formic acid.....	1.2202	1.2212

10. Miscellaneous Salts.—Copper sulfate, sodium sulfate, aluminum sulfate, and potassium carbonate are frequently used where a neutral agent is desired. Copper sulfate reduces the tension of aqueous vapor in benzene solution by 89 per cent and is therefore a very effective material. Sodium sulfate, on the other hand, will reduce the pressure by only 24 per cent (see Table 6). Indeed, this agent is of very little value in eliminating moisture from those solvents, such as benzene or ligroin, where the solubility of water is slight. Aluminum sulfate,²⁸ dried by heating, is claimed to be very hygroscopic.

11. Oxides.—These agents, which combine with water to form either bases or acids, include such substances as calcium oxide, magnesium oxide, barium oxide, aluminum oxide, phosphorus pentoxide, boric oxide, etc. Their efficiency as a class is higher than that of the anhydrous salts, the perchlorates alone being excepted. They have a wide field of usefulness in the drying of substances in the laboratory.

12. Calcium oxide, CaO , is one of the reagents commonly used for drying alcohols, although for removing moisture from air it is less effective than sodium hydroxide (see Table 9). The success of calcium oxide with alcohols is due to the fact that the product of the drying reaction, *viz.*, calcium hydroxide, is insoluble in the organic medium. Hence the reaction is carried to completion. In contrast to this behavior, sodium hydroxide reacts with alcohol, forming sodium ethylate and water. All of the components of this equilibrium²⁹ are soluble in alcohol, making it impossible ever to attain so dry a solvent as when lime is used. Best results³⁰ are secured when the calcium oxide is activated by preheating to 700 to 900° and the fractionating column is packed with small pieces of lime. Inefficiency of calcium oxide, as well as that of copper sulfate, as an air-drying agent may be attributed³¹ to a period of induction required to render it active under dust-free conditions, a belief supported by the absence of any such period when dust is spread over the surface to furnish starting nuclei.

13. Barium oxide for desiccating³² purposes is prepared by low-temperature reduction of barium carbonate with carbon. Although it has a high activity and a large capacity, it cannot be reactivated. The efficiency falls off considerably when in con-

tact with air containing carbon dioxide. In addition to its value in desiccators, this drying agent has special merit at high temperatures, since barium hydroxide is stable up to 1000°C . Barium oxide made in an electric furnace contains carbides which render it unfit for use. The commercial grade recommended by Booth is very cheap and satisfactory.

14. *Aluminum oxide*, Al_2O_3 , is a very effective agent,³³ particularly in desiccators. The commercial material, known as "Activated Alumina," is made from pure aluminum trihydrate. It is reasonably neutral, will absorb 15 to 20 per cent of its weight of water, can be reactivated by heating at 175° for 6 to 8 hr., and does not deteriorate with repeated use. According to the data in Table 5, it is as effective as sulfuric acid in drying air. By reference to Table 8 its excellent reputation as a desiccating agent is seen to be well founded.

15. With *phosphoric anhydride*, P_2O_5 , the highest possible degree of air dryness attainable by chemical reagents is reached. The amount of residual water left in 40,000 l. of air dried over this reagent is only 1 mg. Excellent as this material has proved to be, its suitability for some purposes is nevertheless affected by the presence³⁴ of the lower oxide P_2O_3 . Moisture reacts with phosphorus trioxide, forming hydrogen phosphide which will react with any mercury present to form mercury phosphide, Hg_3P_2 . Pretreatment by passing a stream of ozone through the drying agent while heating in a bath to 300°C . converts the trioxide to the pentoxide. Another disadvantage in the employment of this drying agent is the formation of a sirupy coating on its surface after a little use.

16. *Boric oxide*, B_2O_3 , is made³⁵ by first heating boric acid in a platinum or other metal crucible to about 600°C ., a process attended by considerable frothing. Subsequently the anhydride is dehydrated further at 800 to 900° until all foaming has disappeared. The melt is poured on to an iron plate or marble slab to harden and then placed in a desiccator to cool. The extremely hard and glassy anhydride is powdered before use. Pellets³⁶ of the oxide can be had by pouring the melt into purified carbon tetrachloride which has been chilled to 0° . When used as a drying agent it is found that there is a period of induction before the oxide will act rapidly. This time is less when the final tem-

perature of preparation has not been above 800°. Its efficiency as an air-drying agent is higher than that of sulfuric acid or calcium chloride but somewhat lower than that of phosphoric anhydride or magnesium perchlorate. It is a satisfactory drying agent until its moisture content has risen above 25 per cent of its own weight. Formic acid may be dried by standing over this reagent.

17. Acids and Bases.—With *sulfuric acid* and caustic alkalis the effectiveness likewise may be judged by the vapor pressure of water over the agent. In Table 4 the effect² of temperature and percentage of water on the aqueous tension above these substances is recorded. By comparison with data for calcium chloride (see Table 6) we can conclude that shaking benzene, for example, with 75 per cent sulfuric acid would remove more water than if the solvent had been allowed to stand over calcium chloride.

TABLE 4.—VAPOR PRESSURES OF WATER OVER SULFURIC ACID AND CAUSTIC ALKALIES

Temp., °C.	Vapor pressure, mm. of Hg above				
	NaOH·H ₂ O	KOH·2H ₂ O	H ₂ SO ₄ , 95 %	H ₂ SO ₄ , 75 %	H ₂ SO ₄ , 50 %
0	0.7	0.06	1.6
10	1.2	0.13	3.2
20	0.6	1.8	0.28	6.2
30	0.9	2.4	0.58	11.3
40	1.2	3.3	1.14	20.3
60	10.0	9.1	0.01	3.98	58.0
80	21.0	0.06	12.00	143.0
100	40.0	0.24	32.00	326.0

Concentrated sulfuric acid has the disadvantage of dissolving compounds³⁷ that contain oxygen or nitrogen groups. Even its use in a desiccator is subject to the criticism that under a vacuum of slightly less than 1 mm. it has been found³⁸ to volatilize. A convenient method³⁹ of judging when the effectiveness of sulfuric acid in a desiccator has been spent is to use a solution of 18 g. of barium sulfate in 1 l. of concentrated acid. A precipitate of

barium sulfate will form when sufficient water has been absorbed to render it unfit.

18. The strong caustics, sodium hydroxide and potassium hydroxide, find excellent application in drying amines. Shaking with a strong solution of caustic is often a convenient means for eliminating a large share of water before addition of a solid agent.

19. Metals.—Many of the foregoing considerations apply to metallic drying agents such as the alkali and alkaline earth metals. Thus removal of water from alcohol by sodium metal is not feasible because of the equilibrium between sodium hydroxide and alcohol on one hand and sodium ethylate and water on the other. In cases where no such equilibrium exists, *i.e.*, in benzene or ligroin, removal of water can be practically complete. Metallic calcium might be assumed to be a good reagent for drying, but, owing to the ready formation of calcium nitride^{30,40} when the metal is exposed to air, its use as a drying agent is handicapped by the likelihood of introducing some ammonia. Aluminum amalgam is an extremely effective agent³⁰ for drying alcohols, being the equal of calcium oxide in this respect. It may be made⁴¹ by etching aluminum wire with sodium hydroxide solution and then treating with a dilute solution of mercuric chloride. The amalgam is washed with alcohol and ether. A more active material⁴² is prepared by amalgamating with an alkaline solution of mercuric cyanide. Still another method⁴³ of preparation is to warm thin sheets of aluminum in a solution of mercuric chloride in dry alcohol.

PHYSICAL AGENTS

20. Fractionation.—Ordinary fractionation is sometimes more effective as a means of water removal than is the use of anhydrous salts or other chemical agents. The best method of drying methanol⁴⁴ is to fractionate through an efficient column. The two substances form no constant-boiling mixture and boil far enough apart to insure good separation. By comparison with the use of aluminum amalgam or lime, fractionation permits separation of methanol in as dry or drier state without the loss due to occlusion in the added chemical.

21. Binary and Ternary Mixtures.—Advantage may be taken of the formation of *binary mixtures* of minimum boiling point in

removing water at relatively low temperatures. In drying³ oxalic acid 3 l. of carbon tetrachloride is added to 2 kg. of hydrated acid, and the mixture heated to drive off solvent and water. Mechanical stirring is used to prevent caking of the anhydrous acid, and a separator is employed to return the chloride to the flask. Similarly, cellulose⁴⁵ may be freed from hygroscopic water by pretreatment with acetic acid followed by distillation of added ethylene chloride. Distillation of xylene⁴⁶ in the presence of cellulose or other solid or liquid material will also effect drying. Precipitated silver⁴⁷ after washing with alcohol and anhydrous ether and storing in a desiccator over phosphorus pentoxide was not dried so completely or so quickly as by addition and distillation of benzene. A qualitative judgment of the end of the process in such cases, particularly with solvents in which the solubility of water is very slight, can be had by observing when the distillate no longer runs cloudy. A more accurate opinion can be formed by employing an efficient fractionating column and observing the rise to the boiling point of the anhydrous solvent.

Ternary boiling mixtures have played an important role in drying, not only in the laboratory but also in plants. When benzene is added to 96 per cent alcohol, and the solution distilled, a ternary mixture consisting of 18.5 per cent (by volume) ethanol, 7.4 per cent water, and 74.1 per cent benzene distills at 64.85°. To remove the water from 1 l. of alcohol would theoretically require the addition of 610 g. of benzene. The practical solution⁴⁸ of the problem of avoiding such a large amount of benzene lies in the fact that the distillate on cooling separates into two layers. The lower layer amounts to 16 per cent of the total distillate and has the composition 32 per cent water, 11.6 per cent benzene, and 58.6 per cent alcohol. The upper layer (84 per cent of the distillate) has only 0.5 per cent of water, with 84.5 per cent benzene and 15 per cent alcohol. Since this upper portion is so low in water content, it can be recycled and used as the dehydrating liquid. The lower portion, containing more water, can be dehydrated sufficiently for recycling by shaking with a saturated solution of potassium carbonate. The whole method is frequently referred to as Young's⁴⁹ process. It may be carried out by distilling through a fractionating

column in the conventional manner and continuously returning the upper layer in the separator to the flask or can be made to occur by running the mixture into the upper part of a fractionating column. In this latter instance the temperature at the top of the column is 64.8° for the ternary mixture. Lower in the column it is 68.2° for the binary mixture of alcohol and benzene. Anhydrous alcohol is at the bottom.

Trichloroethylene⁵⁰ can be used in place of benzene as the third component. The ternary mixture boils at 67° . Symmetrical dichloroethylene⁶¹ (b.p. 48.23°) forms a ternary mixture which boils at 44.4° . Its composition is 94.5 per cent of the dichloride, 4.4 per cent alcohol, and 1.1 per cent water. The stereoisomeric dichloroethylene (b.p. 60.25°) also forms a ternary mixture (b.p. 53.8°) consisting of 90.5 per cent dichloride, 6.65 per cent alcohol, and 2.85 per cent water. Both of these dichlorides form binary mixtures with water (b.p. 45.5 and 55.3° , respectively) and with alcohol (b.p. 46.5 and 57.5°).

Work of Atkins and Wilson⁵² can be mentioned as an example of the application of ternary mixtures to the drying of solid compounds. Absolute alcohol was first added to levulose or maltose, and the mixture warmed so that much of the sugar was dissolved. Benzene was then added, and the mixture distilled through a good column. The temperature rose slowly from that of the ternary mixture, 64° , to the binary mixture of benzene and alcohol, 68.25° . Finally the residual alcohol was distilled to effect concentration, after which anhydrous sugar crystallized.

22. Drying with the aid of a constant-boiling mixture is theoretically more effective than drying with salts. For example, the solubility² of water in benzene is approximately 0.07 per cent (0.6 g. per liter) at 25° . The mixture of constant boiling point (69.25°) contains 29.6 mol per cent of water. By calculation all of the water present in 1 l. of benzene at room temperature should come over with the first 7 ml. of benzene distillate. In the ordinary laboratory distillation, *i.e.*, without a fractionating column, such efficiency is impossible. Fractionation is not perfect, and the flask and condenser walls adsorb moisture which is washed down with the first fraction. It is a safe estimate, however, that the solution will be dry by the time that 10 per cent of the benzene has been distilled. This method is

very satisfactory, not only because of the absolute neutrality which prevails during drying, but also because of the freedom from occlusion losses in any solid material. The process is not so effective in the case of solvents that dissolve considerable amounts of water. Ether, for instance, dissolves 1.3 per cent water at 25°. Its constant-boiling mixture (34.15°) with water contains 5 mol per cent which is approximately 1.3 per cent by weight. Distillation would obviously not be practical in this instance. But where the solubility is limited as in the case of benzene, ligroin, or carbon tetrachloride (solubility of water is 0.01 per cent) the method is quite satisfactory.

23. Heat.—Application of heat as a drying agent may be made in one of the standard commercial ovens for heating at atmospheric pressure or under vacuum. Abderhalden's⁵³ simple device for drying small quantities of material is shown in Fig. 1. The outer jacket is heated by the vapor of an organic liquid whose boiling point is near the desired drying temperature. An assembly⁵⁴ for drying in a current of warm air is shown in Fig. 2. An ordinary funnel is inverted over a Buchner funnel so that the stem of the upper funnel can be heated by a flame. Warm or hot gases pass through the crystalline mass on the filter plate. Drying of micro⁵⁵ or semi-micro amounts is accomplished by passing a current of dry air over the solid contained in a small tube. Figure 3 depicts how a stream of dried air is passed over a 1- to 3-mg. sample in a capillary tube. Heat is applied by putting the tube in a metal block, an oil bath, or air bath at a known temperature. Where minute amounts are being examined in the small capillary tube, the melting point can be determined on the dried sample without transferring it to another capillary. Such methods are necessary when working on a micro scale (see Sec. 181).

In drying a viscous material or sirup in a vacuum oven, a thin film is necessary if completeness and rapidity are desired. An ingenious method,⁵⁶ used in the quantitative determination of moisture, is to put a drop of the sample between two metal (silver) plates each 10 by 15 by 0.0007 cm., place them on a piece of warm (60 to 70°) plate glass, and then roll them with a rubber-faced roller such as is used to mount photographs. This treatment spreads the drop and removes part of the moisture. More

spreading is accomplished by subsequent use of a wooden roll. The plates are next pulled apart and dried in a vacuum oven at 70°C . Constant weight is attained in 2 to 4 hr., which is a considerably shortened time over the ordinary method. The plates are weighed before the rolling and after the drying. To avoid absorption of water during weighing, the plates with the material between them are always pressed together.

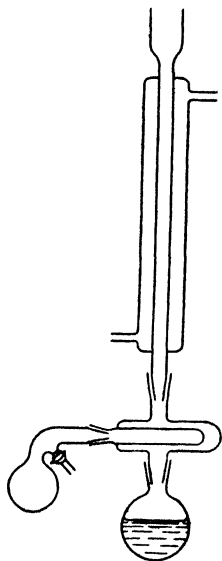


FIG. 1.—Abderhalden vacuum drying apparatus.

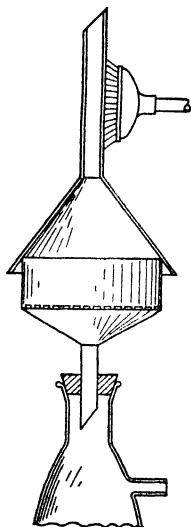


FIG. 2.—Arrangement for drying precipitates on a Buchner funnel.

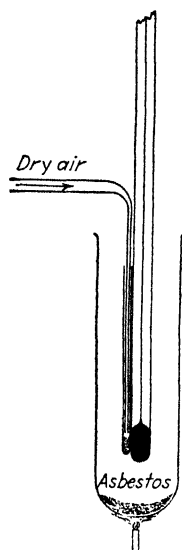


FIG. 3.—Micro-drying apparatus for use with 2 to 3 mg. of material in a capillary tube.

24. Cold.—Freezing has also been employed to remove moisture from air. In measurements⁵⁷ of the ion age better drying was had by cooling in liquid air than was obtained with phosphorus pentoxide. Carbon dioxide snow (-72°) reduces¹ the moisture in air to 0.016 mg. per liter, while salt and ice (-21°) lower it to 0.045 mg. Both of these values are better than that found with fused sodium hydroxide. Ether⁵⁸ may also be freed from some of its water by cooling to -78° , but this method cannot usually be employed for drying compounds dissolved in

ether, because the compounds themselves will precipitate out at this low temperature.

25. Adsorption, Absorption, and Extraction.—Completely dry cotton, wool, or silk is almost as efficient a drying agent²⁴ as is phosphoric anhydride. Over calcium chloride 1.2 to 2.3 per cent of the moisture remains adsorbed. They are therefore more powerful dehydrating agents than calcium chloride. Their capacity is obviously not very great, because drying depends upon adsorption on a solid surface. This phenomenon of *adsorption* on solids is of common occurrence in the laboratory. For example, ether or benzene that has been dried over sodium in one vessel will give off more hydrogen when transferred to another container and treated with fresh metal. The water present on the walls of ordinary laboratory glassware after drying in an oven at 100° may easily be seen by heating and observing the moisture which condenses above the heated portion. If dryness is a factor in any reaction such as with the Grignard reagent, organoalkali metal compounds, or substances containing labile halogen, the container should always be rinsed with a dry solvent before adding the main body of the liquid. This method⁵⁹ of washing with dry liquid ether has been shown to remove about half as much moisture from the wall of a flask as is done by heating to 304° for 2 hr.

Drying by *absorption* makes use of the great affinity that liquids have for moisture on the surfaces of solids. In the quantitative determination⁶⁰ of moisture in coal by shaking with methanol, the coal is first ground to pass a 60-mesh screen, then weighed, put in a separatory funnel, and shaken with methanol for half a minute. The amount of water removed from the coal is measured by a density determination of the alcohol. Analysis showed 32.5 and 30.5 per cent moisture as determined by this method. The corresponding values found by drying at 108° were 31.8 and 30.9 per cent. Acetic acid, acetone, or ethanol may also be used as solvents. The method is applicable to any solid that does not dissolve in the liquid used. Less volatile hygroscopic liquids such as glycerol may be used for removing moisture from gases by a scrubbing process.

Extractions have been employed to free solvents from some of the water that they hold. As early as 1883 Goering⁶¹ patented

a method for obtaining concentrated acetic acid by extracting with low-boiling esters such as ethyl acetate. The ester was subsequently distilled, leaving the acetic acid in more or less anhydrous condition. An improvement in this process is the addition of petroleum^{62,63} to the extracting liquid. More recently propyl, isobutyl, and *n*-butyl alcohols⁶⁴ have been partially dried by extraction with an approximately equal volume of carbon tetrachloride. The remainder of the water is removed when the tetrachloride is distilled.

RELATIVE EFFICIENCIES OF DRYING AGENTS

26. *Relative efficiencies of drying agents* may be judged in a number of ways. One standard method is to pass air, previously saturated with water vapor, at a rate of 1 to 3 l. per hour through the drying agent at 25°. A tube of phosphorus pentoxide collects the moisture not absorbed in the first vessel. The amount of water caught by the pentoxide is calculated as

TABLE 5.—EFFICIENCIES OF AGENTS IN DRYING AIR

Drying Agent	Milligrams of Water per Liter of Air
Cooling to -194°.....	1.6×10^{-23}
P ₂ O ₅	2×10^{-5}
Mg(ClO ₄) ₂	5×10^{-4}
Mg(ClO ₄) ₂ ·3H ₂ O.....	2×10^{-3}
KOH (fused).....	0.002
Al ₂ O ₃	0.003
H ₂ SO ₄	0.003
CaSO ₄	0.004
MgO.....	0.008
CaBr ₂ at -72°.....	0.012
Cooling to -72°.....	0.016
CaBr ₂ at -21°.....	0.019
Cooling to -21°.....	0.045
CaBr ₂ at 25°.....	0.14
NaOH (fused).....	0.16
CaO.....	0.2
CaCl ₂	0.14 to 0.25
H ₂ SO ₄ 95.1 per cent.....	0.3
CaCl ₂ (fused).....	0.36
ZnCl ₂	0.8
ZnBr ₂	1.1
CuSO ₄	1.4

milligrams of moisture per liter of air. Table 5 gives the results of a number^{1,2,26} of these investigations.

Another method is to observe the freezing-point depression of an organic liquid in contact with a drying agent and compare it with the value for the fully saturated or absolutely dry solvent. Tables 6 and 7 contain data for benzene⁶⁵ and nitrobenzene.⁶⁶ This method is more in agreement with the frequent practice of adding a drying agent to an organic solvent.

TABLE 6.—EFFECT OF DRYING AGENTS ON FREEZING POINT OF BENZENE

Benzene	Freezing point, °C.	Lowering of freezing point, °C.	Tension of aqueous vapor, mm. of Hg
Saturated with water.....	5.393	0.100	6.73
Over Na ₂ SO ₄	5.420	0.073	5.11
K ₂ CO ₃	5.454	0.039	2.62
CuSO ₄	5.482	0.011	0.74
CaCl ₂	5.484	0.009	0.61
NaOH.....	5.491	0.002	0.13
P ₂ O ₅	5.493	0.00

TABLE 7.—EFFECT OF DRYING AGENTS ON FREEZING POINT OF NITROBENZENE

Nitrobenzene	Freezing point, °C.	Lowering of freezing point, °C.	Pressure of water, mm. of Hg
Saturated with water.....	5.158	0.511	6.60
Over Na ₂ SO ₄	5.346	0.323	4.31
SrCl ₂	5.534	0.135	1.92
H ₂ C ₂ O ₄	5.627	0.042	0.60
P ₂ O ₅	5.669	0.00

Of considerable interest is the comparison of efficiency⁶⁷ by observing loss of moisture when various substances are placed in desiccators over different agents. In Table 8 the water loss and drying time at 25° are given. Results comparable to these data were also obtained with coffee. Other tests³³ with hydrated copper sulfate over alumina, phosphoric anhydride, and calcium

chloride showed that constant weight was not reached over any of the desiccants until 18 to 21 days. The total amounts removed were 42.8 per cent by alumina, 41.5 per cent by phosphoric anhydride, 42 per cent by sulfuric acid (96 per cent), and 43 per cent by calcium chloride. The low result over pentoxide is ascribed to poor diffusion of air through phosphoric acid formed on the surface. In a second series of tests which included mixed barium and magnesium perchlorates, activated alumina was best, and the perchlorates were poorest. All of the foregoing experiments were made at atmospheric pressure. It is obvious that porosity is a large factor in the performance of a drying agent in a desiccator.

TABLE 8.—LOSS OF WATER IN A DESICCATOR

Time, days	Flour dried over			CuSO ₄ ·5H ₂ O dried over		
	Al ₂ O ₃ , %	H ₂ SO ₄ , %	CaCl ₂ , %	Al ₂ O ₃ , %	H ₂ SO ₄ , %	CaCl ₂ , %
1	8.42	8.42	8.47	14.11	15.08	15.22
2	9.51	9.56	9.21	18.76	19.47	16.84
3	10.30	10.33	10.06	23.73	25.51	21.31
4	10.67	10.61	10.35	28.11	28.74	25.40
6	11.21	11.13	10.75	29.43	29.45	29.32
7	11.46	11.33	10.96	29.53	29.54	29.42
11	11.75	11.64	11.15			
13	11.75	11.64	11.15	29.53	29.54	29.42

Efficiency of a catalyst for conversion of carbon monoxide to carbon dioxide is appreciably affected by water vapor. Accordingly, the activity of various drying agents can be measured⁶⁸ by observing the amount of conversion after passing moist air containing carbon monoxide through the desiccant. The catalyst was placed on a wire disk directly above 15 ml. of the drying agent (12 to 14 mesh) contained in an upright glass tube. Air with moisture content equal to 50 per cent saturation at 20° and carbon monoxide concentration of 1 per cent by volume was passed through the tube at a velocity of 200 l. per hour. The amount of carbon dioxide in the effluent gas was measured on a carbon monoxide indicator sensitive to 0.01 per cent. The

results given in Table 9 show that activated alumina was the most active with respect to life and weight of water absorbed.

TABLE 9.—EFFICIENCY OF DRYING AGENTS AS MEASURED BY LIFE OF CATALYST FOR CARBON MONOXIDE TO CARBON DIOXIDE CONVERSION

Drying agent	Life, min.	Water absorbed		Weight of drying agent, grams
		Grams	Per cent	
Al ₂ O ₃	71	3.04	27.2	11.2
Mg(ClO ₄) ₂	56	2.40	32.0	7.5
CaCl ₂	56	2.40	21.8	11.0
BaO.....	26	1.11	3.7	30.0
CaCl ₂ and soda lime.....	20	0.86	9.05	9.5
BaO ₂	16	0.69	2.6	27.0
Al ₂ (SO ₄) ₃	13	0.56	7.6	7.4
NaOH (pellets).....	6	0.258	1.7	15.2
Na ₂ SO ₄	4	0.172	1.5	11.6
MgCl ₂	2	0.086	1.1	7.8
MgSO ₄	1	0.043	0.52	8.3
CaO.....	1	0.043	0.21	21.2

Some of the foregoing methods, *e.g.*, freezing point, may be used as *tests for dryness*. Another common method is the measurement of variation of density with water content which in the case of alcohol is the standard guide. Osborne, McKelvy, and Bearce³⁰ state that calcium carbide, copper sulfate, and metallic calcium give no indication of water in alcohol whose density at 25° is below 0.78510. Anhydrous alcohol at the same temperature has a density of 0.78506. That of 99 per cent alcohol is 0.78814. Organometallic compounds are frequently useful as tests. Bent and Irwin⁶⁹ preferred the green sodium fluorenone to the blue-colored sodium benzophenone, both made from reaction of the ketone with sodium amalgam, as a drying agent for solvents that do not react with water. Zinc diethyl has also been used as a sensitive test, although Mendeleef⁷⁰ found that it was not satisfactory for alcohol. Where the solvent is unreactive toward the Grignard reagent, this organometallic compound may be employed.

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CHAPTER II

THE MELTING POINT

27. For ordinary purposes the melting point is defined as the temperature at which a solid material, in contact with air, changes under equilibrium conditions to the liquid state. It is not a true triple point, for air as well as its own vapor is in contact with the substance. The difference, however, is very slight,¹ amounting to only 0.003° in the case of benzene, and can be neglected in the usual measurements of an organic laboratory. Of all methods used the capillary tube is by far the most common and convenient. It has the further advantage of requiring very small amounts of material. Small as is this quantity it may be further reduced by employment of one of the various micro methods which are now at the chemist's disposal. If a larger sample is available, more exact knowledge of its purity may be had by resort to the curve method. These procedures and other miscellaneous ones form the subject matter for this chapter.

THE CAPILLARY-TUBE METHOD

28. General Directions.—Thin-walled capillaries, about 1 mm. in diameter, are made by heating and drawing out tubing that has previously been washed with distilled water and dried. For fibrous or waxy compounds the tubing may have to be a trifle larger. The capillaries are sealed at one end and loaded by pressing the open end into the finely powdered material, followed by tapping or rasping to force the sample to the bottom. The length of solid in the tube need not exceed 2, and should preferably be only 1, mm. The tube is next inserted in a suitable bath (see Fig. 5) with the sample adjacent to the thermometer bulb, and the whole heated until melting occurs. The rate of heating should be regulated so that the rise in temperature does not exceed 1° per minute in the vicinity of the melting point. Readings are usually observed on a thermometer ranging from 0 to 360° . The melting point is taken as the point where the

first appearance of liquefaction occurs. If the sample is pure, the range from the temperature of initial to complete melting should not exceed 0.5° and may well be less. The thermometer reading at the melting point is frequently corrected for the exposed stem (see Sec. 44), in which case it is given as $^{\circ}\text{C. corr.}$ A detailed discussion of the factors involved in the capillary-tube method is given in the following sections.

29. The Necessity for Clean Tubing.—If tubing from which capillaries are constructed is not washed, *alkali and products of devitrification* remain on the surface of the glass and may interfere with securing accurate results. Presence of alkali has been shown² to lower the melting point of compounds that have a free aldehydic or ketonic group capable of undergoing mutarotation. Table 10 gives the values obtained in ordinary tubes as compared with results in capillaries that have been made from tubing cleaned with distilled water. The letter *S* refers to the temperature at which sintering begins; *F* denotes the temperature of fusion.

TABLE 10.—LOWERING OF FREEZING POINT IN UNWASHED CAPILLARIES

Compound	In ordinary tube		In dealkalized tube	
	<i>S</i> , $^{\circ}\text{C.}$	<i>F</i> , $^{\circ}\text{C.}$	<i>S</i> , $^{\circ}\text{C.}$	<i>F</i> , $^{\circ}\text{C.}$
Glucose.....	133	143–146	142	146–147
2, 3, 4, 6-Tetraacetyl- α -glucose.....	105	110–112	111	112–113
Fructose <i>B</i>	95	98–105	102	104–105

Dust or products of devitrification on the glass surface may cause an error of 4 to over 10° with certain solids which are very finely divided. Originally this result was ascribed³ to differences in surface tension between solid and melted substance, and equations for expressing the effect mathematically were proposed. Subsequently it was found⁴ that the effect disappeared when the glass tubing was washed before the capillaries were made. Melting points of phenacetin, antipyrin, and salol have been observed to be 4, 5, and 7° respectively lower in unwashed tubes than in cleaned ones. When mannite, carefully purified and finely ground, was observed under the microscope, small drops formed

on the walls of the unwashed tubes as low as 150° , whereas in cleaned tubes the melting point was sharp at 165° .

30. The Rate of Heating.—Time must be allowed for transfer of heat through the glass wall of the capillary tube to the organic solid and for dissipation of the heat of fusion. This time is reduced to a minimum by using thin-walled tubing. Because observations of thermometer and sample are not simultaneous, the rate of heating must be slow enough to make the error from this source negligible. An interesting effect from too rapid heating has been recorded by Letsche⁵ who observed that the melting point of glycocholic acid could be changed from 132 to 178° by varying the rate of heating. A rise of 1° a minute at the melting point is about the maximum rate at which it is possible to make satisfactory observations of the change of state. In the apparatus of Francis and Collins⁶ for very exact determinations (see Sec. 38) the rate during fusion was 0.1° in 4 min.

31. Relation of the Purity to Melting Point.—The *sharpness* with which a compound melts is assumed to be an index of its purity. Fortunately this assumption is usually correct when apparatus and manipulation are satisfactory. A rare exception occurs when the material under investigation is a eutectic mixture. Trouble is sometimes experienced with the presence of a constant amount of impurity which causes the temperature to fall a trifle short of that usually attainable. By recrystallizing from another solvent this error may frequently be avoided. Indeed, as a general precaution the observation of the melting point of a material crystallized from two different solvents can be highly recommended as a check on purity. If this method fails to produce a sharp melting point, the product should be distilled, sublimed, steam distilled, extracted, treated with decolorizing carbon, chromatographically adsorbed, or otherwise handled in a further attempt to eliminate the trace of impurity. Occasionally, mixtures melt as sharply as a single material. A molecular compound which resisted attempts at separation by recrystallization from different solvents was reported by Kohler and Mydans.⁷ Oxotetraphenylpropanol (m. p. 159°) with another mol of tetraphenylpropenone (m.p. 154°) formed an addition compound melting sharply at 162° . It was separated by subjecting it to a chemical reaction which differentiated between the components.

While the sample with *highest melting point* would obviously represent highest purity for any given material, it does not follow that the highest melting point given in the chemical literature represents the purest specimen. Tseng⁸ reports discrepancies that amounted to more than 2° with different types of apparatus and differences of as much as 1° with different observers using the same apparatus. These figures represent probably the maximum amount of divergence. Francis and Collins⁶ state that they seldom differed from each other by more than 0.2° using an ordinary apparatus, a bath of sulfuric acid heated by means of a Bunsen flame, and a thermometer on which 1 mm. of scale length was equivalent to 1° . With a better apparatus (see Sec. 38), carefully prescribed conditions, and a thermometer with a more open scale, they found a difference among observers no greater than 0.03° . This value probably represents the maximum amount of reproducibility so far attained by this method. It is clear that values recorded in the literature are not always accurate and that the specimen reported to have the highest melting point need not necessarily be the purest unless accompanied by full description of precautions observed.

32. Mixed Melting Points.—Another common assumption is that mixtures of unlike substances will melt lower than the individual members. So general is this belief that failure of a mixture to show a depressed melting point is taken as a criterion of the identity of two substances. Again, it is fortunate that the rule is of such wide applicability. Such a generality should not obscure the

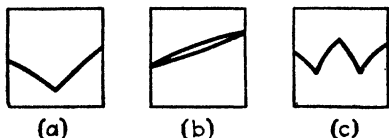


FIG. 4.—Temperature-composition diagrams showing typical behavior upon solidification.

fact that systems do occur in which no change or an elevation of melting point is realized. This statement is merely equivalent to saying that the melting points of all mixtures of organic compounds cannot be represented by the diagram shown in Fig. 4a in which the substances *A* and *B* crystallize from solution substantially uncontaminated with the other until the eutectic composition is reached. Systems of mixed crystals (Fig. 4b) or of those in which compound formation occurs (Fig. 4c) are equally possible. That the rule of mixed melting points

is not free from exceptions may be seen from data in Tables 11⁹ and 12.¹⁰ Melting points of mixtures of isoamyl- and active amyl-ethylbarbituric acids¹¹ have been shown to lie between the

TABLE 11.—MIXED MELTING POINTS WHICH ARE UNRELIABLE CRITERIONS OF IDENTITY

Compound	Melting point, °C.	Melting point of mixture, °C.
Tribromomesitylene.....	223	} 224–225
Tribromopseudocumene.....	229–230	
Tetrabromo- <i>o</i> -xylene.....	258–260	} 251–253
Tetrabromo- <i>m</i> -xylene.....	247–248	
Tetrabromo- <i>m</i> -xylene.....	247–248	} 248–250
Tetrabromo- <i>p</i> -xylene.....	248–250	
Thiophene picrate.....	134	} 140–141
Thionaphthene picrate....	149	
Thiophene picrate.....	134	} 134
Naphthalene picrate.....	151	
Bromohydroxyhydrindene.....	130–131	} 127–128
Chlorohydroxyhydrindene.....	124–125	

TABLE 12.—MIXED MELTING POINTS WHICH SHOW LITTLE OR NO DEPRESSION

Picrates of Trimethylnaphthalene	Melting Point of Mixture, °C.
1,2,3- (142.5°) and 1,4,5- (144.5°).....	142–144
1,4,5- (144.5°) and 1,2,4- (147.5°).....	144–146
1,2,3- (142.5°) and 1,2,4- (147.5°).....	142–143
1,2,6- (120–5°) and 1,3,8- (122°).....	121–122

values (154 and 134°, respectively) for the two components. A smaller difference exists for mixtures of 3-bromo-5-iodo-4-amino-benzophenone¹² and 3,5-dibromo-4-aminobenzophenone whose melting points are 145.9 and 146°, respectively, and whose mixed melting points throughout the entire composition diagram do not fall below 144.6°. In cases of doubt, resort may be had to the melting point of a derivative. Thus, 2,6-dichloro-4-bromo-3-hydroxybenzaldehyde¹³ and 4,6-dibromo-2-chloro-3-hydroxybenzaldehyde both have melting points of 104 to 105° and the mixtures of the two in the ratio of 1:1, 1:3, and 3:1 show slight,

if any, lowering. Melting points of mixtures of their derivatives, however, show considerable differences as indicated in Table 13. A similar thing was found with 2'- and 3'-methylnaphthafluor-

TABLE 13.—MIXED MELTING POINTS OF DERIVATIVES OF HYDROXYBENZALDEHYDE COMPOUNDS

Derivative	Melting points of varying percentage mixtures of dichloro- in dibromo-compound, °C.					
	0 %	8-10 %	49-51 %	74-75 %	90-91 %	100 %
Ethyl ether.....	81.5	80	72-73	70-71	68.5	66.5
Anil.....	63.5	63	60	59.5	59-59.5	59
Oxime.....	152	141-145	135-140	133-134	132	128.5
Phenylhydrazone.....	113.5	113-114	117-118	118-119	120	122

enes¹⁴ whose melting points, separately within a few degrees of each other, are not appreciably depressed by the other's presence. The ketones obtained by oxidation likewise melt near each other, but their mixtures showed large depressions.

33. Decomposition at the Melting Point.—For compounds that melt with decomposition a characterization by melting point is more difficult. The capillary tube should be inserted in the bath when the temperature is only a few degrees below and preferably at the melting or decomposition point of the material. Several approximations have to be taken in order to find this point. In the case of glycocholic acid, Cortese and Bauman¹⁵ characterized the compound by noting the temperature at which the specimen sintered and foamed completely within 30 sec. The Dennis¹⁶ bar can be used advantageously with compounds that decompose on melting, since the behavior of the crystals when dropped on the hot copper surface can be observed easily (see Sec. 52).

34. Multiple Melting Points.—Compounds that exist in two or more modifications will be observed to fuse, solidify, and then melt again at a higher temperature. These effects are well illustrated by the triple melting points of triglycerides.¹⁷ The lowest value, that of a glassy solid, was found by immersing the rapidly cooled glyceride in a bath where it just melted and resolidified. A second melting point was determined in the

same way after a number of trials to find the approximate temperature. The highest melting point was determined in the usual manner. Trilaurin, for example, melted at 15, 35.0, and 46.4°. Values for three different states of tristearin were 54.5, 65.0, and 71.5°. The phenomenon of triple melting points is common to all triglycerides.

35. Relation of Melting Point to Structure.—The symmetrical isomer of a given pair will, in general, have the higher melting point. This fact has been shown to be true in the case of a number of synthetic glycerides¹⁸ (see Table 14; consult also

TABLE 14.—MELTING POINTS OF SYMMETRICAL AND UNSYMMETRICAL GLYCERIDES

Glyceride	Melting point, °C.	Refractive index 70°	Solubility, g. per 100 ml. of alcohol at 23°
α -Capryl- α' , β -dilaurin.....	32.6	1.43640	9.00
β -Capryl- α , α' -dilaurin.....	38.8	1.43705	3.02
α -Acetyl- α' , β -distearin.....	55.2	1.44045	0.43
β -Acetyl- α , α' -distearin.....	62.0	1.43970	0.06

Table 52). A higher melting point is usually associated with higher refractive index and lower solubility in water.

36. Apparatus.—Many forms of *liquid baths* have been proposed for use with the capillary-tube method. These may be classified under three general types, *viz.*, the test tube (test tube, beaker, or flask), shown in Fig. 5 with stirring rod and thermometer supporting the capillary; the Thiele tube (Fig. 6) which is heated on the side by gas or electricity so as to induce gravitational circulation of liquid as is done in hot-water heaters; and the double-bath apparatus (Fig. 7) containing a test tube which reaches to within 1 cm. of the bottom of the 250-ml. flask and insulates the thermometer and sample from convection currents. In the simplest form of each of these types the capillary tube is attached to the thermometer by a rubber band (cross section of rubber tubing) or a platinum wire. A capillary tube can be made to adhere loosely to the thermometer without these supports by merely wetting the upper portion of the capillary with

the bath liquid or more firmly by placing a glass rod¹⁹ against the thermometer for the entire length above the bulb and setting the capillary in the indented portion where thermometer and rod touch. Even the most vigorous stirring fails to dislodge it from this position. The inconvenience of having to remove the thermometer to insert a new capillary can be dispensed with in the first two types by sealing a section of tubing at an angle to

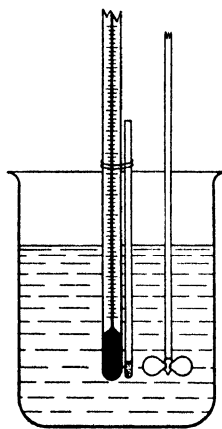


FIG. 5.—Simple melting-point apparatus made from a beaker, thermometer, and stirrer.

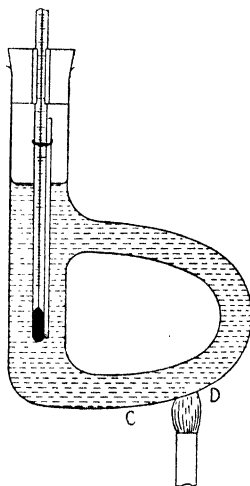


FIG. 6.—Thiele melting-point apparatus.

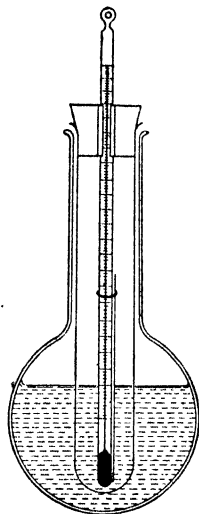


FIG. 7.—Double-bath melting-point apparatus.

the apparatus so that the melting-point capillary can be inserted with the sample end touching the thermometer bulb (see Fig. 8). This tubing may be of capillary dimensions so that the melting-point tube slides through it conveniently or may be large enough to carry a cork through which the sample tube is passed.

37. *The Thiele apparatus* suffers from insufficient stirring. Berl and Kullmann²⁰ found that the melting point of fluorene varied from 108.5 to 116.9° depending on the position of the thermometer in the tube and the point where heat was applied, *e.g.*, at *C* or *D* (Fig. 6). For phthalimide the melting points varied from 224.1 to 239.5°. These erratic results were responsi-

ble for their interest in developing the copper block (see Sec. 40). Conte²¹ overcame this difficulty by blowing or sucking a current of air through a 0.5-mm. orifice (illustrated in Fig. 9) at such a rate that it was just possible to count the bubbles. The tube containing the orifice must project far enough into the side arm

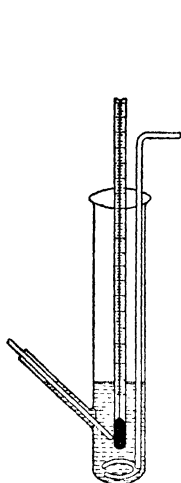


FIG. 8.—Melting-point apparatus with a removable capillary tube.

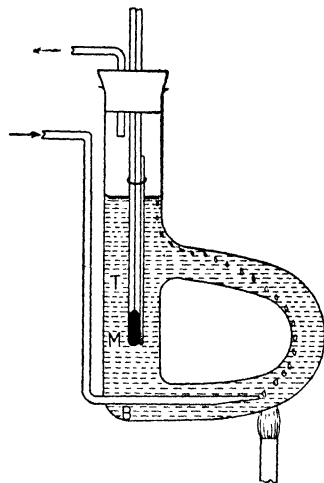


FIG. 9.—Stirring a Thiele melting-point tube with a current of air.

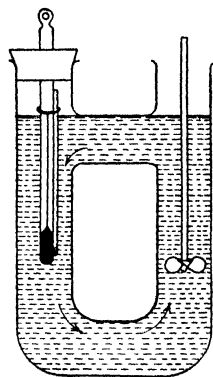


FIG. 10.—Modified Thiele melting-point tube with mechanical stirrer and total immersion thermometer.

to prevent the bubbles from taking a wrong path. Results in this modified Thiele tube are compared with those in the ordinary form in Table 15. The letters *T*, *M*, and *B* refer to the top, middle, and bottom of the tube, respectively. The values show that the temperature in the tube is much more uniform

TABLE 15.—TEMPERATURES IN THE THIELE TUBE IN DEGREES CENTIGRADE

Temperature at	Modified Thiele tube				Ordinary Thiele tube			
	50	100	150	200	50	100	150	200
<i>T</i>	50	100	150	200	50	100	150	200
<i>M</i>	50	99.8	149.5	199.2	42	89	138	187
<i>B</i>	49.9	99.5	148.8	198.0	36	76	122	168

than before and that the position of the capillary tube with respect to the thermometer should therefore be less critical. Avery²² has reconstructed the Thiele tube so that a stirrer can be put in the side arm (Fig. 10), and Markley²³ has employed a high-speed turbine stirrer for the same purpose. More recently, Hershberg²⁴ has made valuable improvements by placing a total immersion thermometer and tubes in an adiabatic zone in which the deviation in temperature does not exceed 0.025° . Construction is simplified so that tubes can be inserted and withdrawn quickly. The stirrer turns easily in an ordinary commercial ball-bearing assembly 2.2 cm. in outside diameter with a 0.94-cm. hole, in which is inserted a piece of rubber tubing whose inside wall is moistened with glycerol to serve as a lubricant for the 6.5- to 7-mm. stirrer shaft.

38. *Refinements in other types of apparatus* permit their use with greater accuracy. Steiger²⁵ also sought to avoid stem corrections by using a set of total-immersion thermometers. His apparatus is similar to that shown in Fig. 8 with the addition that the top is entirely enclosed, the stirrer is moved mechanically up and down, and the fumes are drawn away as they escape about the opening for the stirrer. Francis and Collins⁶ have raised the mechanics of reading to a high state of perfection. The bath was a cylindrical tube 9 cm. long by 5 cm. in diameter, which contained a fused-in plate-glass window for improving visibility. The paraffin was heated by an internal electric coil and stirred with the aid of a constant-speed motor. The capillary was viewed through a telescope (magnification 6) through the eyepiece of which could also be seen the thermometer scale readings, a fact made possible by a periscope device mounted on a rack and pinion. Hence alternate gazing at sample and thermometer was avoided. Small 12-volt lamps, suitably screened, illuminated scale and sample, the latter so that it could be viewed by reflected or transmitted light.

Considerable attention was paid by them to the process of making the determination. The approximate melting point was first determined, after which the material was allowed to resolidify, and the accurate value determined by raising the bath temperature rapidly to within 1° of the melting point. The rate was then slowed to 0.1° every 4 min., and the temperature

of melting taken at the point where a clear liquid first appeared on the surface of the solid. Under these conditions the melting point by different observers did not vary more than $+0.03^{\circ}$. The thermometer used for the determination was graduated in 0.1° (4.6 mm. of scale length corresponding to 1°) and was calibrated by partial immersion (see Sec. 44) to a depth of 2.5 cm.

39. As a *liquid for melting-point baths* one may use concentrated sulfuric acid for determinations as high as 280 or 300° , although its tendency to fume increases at these high temperatures. When seven parts by weight of sulfuric acid (1.84) and three parts of potassium sulfate are boiled together for 5 min. (they must be well stirred to prevent formation of two layers which then boil with explosive violence), a liquid²⁶ is obtained which is transparent at ordinary temperatures and can be heated to 325° without boiling. Six parts of acid and four of sulfate form a mixture that is a soft mass at ordinary temperatures but can be heated above 365° . The vapors above this mixture in an apparatus of the double-bath type were so slightly acid that a rubber band could be used on the thermometer to hold the tube in place provided the band was 1 to 2 cm. above the surface of the bath. When a bath has not been heated for a few weeks it should be boiled for some minutes before using at temperatures above 300° . All sulfuric acid baths can be clarified by boiling with a few drops of concentrated nitric acid or with a few crystals of potassium nitrate.

Phosphoric²⁷ may be used in place of sulfuric acid. Between 100 to 300° , steam is constantly driven off so that mechanical stirring may be eliminated. At 100° the phosphoric acid begins to lose moisture, and at 213° conversion to pyrophosphoric acid begins. Upon cooling, if the temperature of the bath has not exceeded 200° , about 10 per cent of water is stirred in below 100° so that the bath is ready for use again. More water must be added if the bath has been heated to 300° . Potassium nitrate can be added to clarify the acid when necessary. One beaker of phosphoric acid has been reported to have lasted for over a year.

Paraffin or Nujol cannot be heated to a temperature so high as is possible with the acids. Vegetable oils are frequently satisfactory, particularly if compounded with 1 per cent of hydroquinone.²⁸ Fused zinc chloride²⁸ can be used for temperatures

from 360 to 600°, but it must be poured out on a tile to cool lest its expansion break the container. Mixtures of potassium nitrate²⁹ with 45 per cent by weight of sodium nitrate melt as low as 225.7°. A ternary mixture³⁰ of 20 equivalents of sodium nitrate, 45 per cent potassium nitrate, and 35 equivalent per cent calcium nitrate [$\frac{1}{2}\text{Ca}(\text{NO}_3)_2$] melts at 175°.

40. Copper Blocks.—Copper blocks are very convenient because they can be used over wide ranges of temperature without danger of producing fumes or of fouling the liquid. Originally devised by Thiele,³¹ they have been greatly perfected and made into one of the most convenient pieces of apparatus in the laboratory. Copper is ideal for this purpose, since its high heat

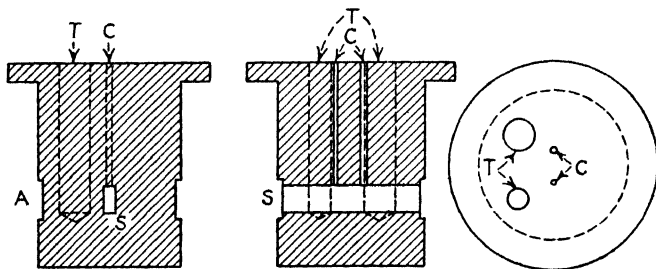


Fig. 11.—Berl and Kullmann copper block for melting-point determinations.

conductivity virtually eliminates errors that might arise from lack of uniform temperature. The machined parts of an apparatus are as follows:

1. A copper block 52 to 70 mm. long by 38 to 50 mm. in diameter. Although the literature calls for use of a circular block, students in the institute laboratory have constructed them from square sections of copper with considerable simplification in drilling the necessary holes so that they meet properly. The block has:

2. An upper circular rim, approximately 3 mm. thick and extending 8 mm. beyond the body of the block, which serves to support the apparatus in the ring stand. In the circular blocks this support is made by turning down a large piece of copper in a lathe. In the square blocks a holder can be made by fastening copper rods or screws into holes drilled in the sides. Thiele, indeed, used a single rod support for his block and fastened it in the ordinary laboratory clamp. Short sections of angle brass, attached by screws at the top on two sides, also make good hooks with which to hang the apparatus in an iron ring or asbestos board. From the top of the block are bored:

3. One or more holes (marked *C* in Fig. 11) 1.5 to 2.0 mm. in diameter near the center of the block so that they meet the transverse section. A little to one side and as conveniently near as possible are located the

4. Thermometer holes (marked *T* in the illustration) which are 6 or 8 mm. in diameter and extend far enough into the block that the middle of the thermometer bulb will be at the same level as the sample.

5. A transverse slit²⁰ (labeled *S*) 3 by 7 mm. is cut through the block so that the capillary tubes will drop exactly into its middle. This centering of the capillary is important in aiding visibility, since light will then pass on both sides of the melting-point tube. The opening is rectangular rather than circular in order to reduce the distance necessary to radiate heat from copper wall to capillary tube. Construction of this slit is a most troublesome operation. With the telescope arrangement of Walsh³² for viewing the capillary it is possible to use a circular opening 3 mm. in diameter, thereby simplifying this construction. It is also easier to drill holes correctly centered when a square block is used.

6. A shallow cut-in section *A* completes the mechanical work on the metal. A strip of mica can be wound about the block at this point in order to prevent access of air through the slit yet retain visibility.

41. *Heating* the block is done conveniently by gas. The circular forms can be wrapped, first with asbestos and then with resistance wire (Monsch³³ used 6 m. of chromel wire having 8 ohms per meter resistance) so that electrical heating with rheostat control can be used.

42. *To observe the melting point* a light, conveniently shaded, on the far side of the block is indispensable. Lenses are great aids to accurate observation. Friedel³⁴ made a marked improvement by using a lens L_1 on the far side (see Fig. 12) to focus the rays of light through the slit and another lens L_2 on the near side to enlarge the image on a ground-glass plate *G* so that the change in state upon melting could be seen easily even though the observer was several feet away. The arrangement has the single disadvantage that color changes and decompositions are not detected easily. Walsh³² trained a 50-power microscope on the opening which permitted direct observation of the sample. Use of this microscope allows observation of the melting point of a single crystal, thereby making it applicable to micro determination of the melting point (see Sec. 46). As stated before, the rectangular slit can be replaced by the more conveniently bored hole, 3 mm. in diameter, when this attachment is used. Walsh has described a very compact unit for this apparatus which is easy to keep in adjustment even when used by a large class of

students. It is obvious that micro boiling points by Siwoloboff's method (see Sec. 54) can be observed in this same apparatus.

43. Radical changes in the form of the copper block have been effected by Linström³⁵ (see Fig. 13). A large hole, 10 mm. by 42 mm. long, is drilled in the center of a 45- by 55-mm. block. The open end of the hole is expanded to 20 mm. for a distance of 7.5 mm. to accommodate a copper plug which, in turn, sup-

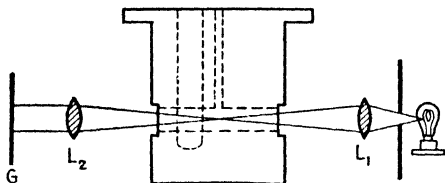


FIG. 12.—Copper block with lenses and ground glass plate for melting-point observations.

ports from a rod the small closely fitting platform *P*. The upper surface of this platform is on a level with the bottom of the transverse opening *A-B*. The air space under the platform is to help maintain a uniform temperature. Thermometer and melting-point tubes rest on the platform, and the openings in the top of the metal plug through which the capillaries are inserted are inclined just enough to insure that the sample will be close to the thermometer. All transverse openings (6-mm.

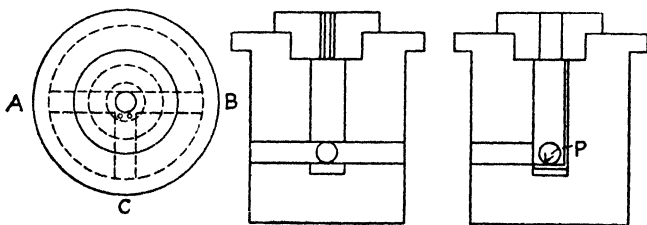


FIG. 13.—Copper block of Linström.

diameter holes) are closed by mica or glass. The triple opening permits a variety of lighting effects and observation angles. Ordinary procedure is to illuminate from both *A* and *B* and observe through *C*. A great advantage of this apparatus is that comparison melting points may be made simultaneously. The time required for a single determination is comparatively long.

44. Thermometers.—A *total-immersion* thermometer means that the thermometer has been calibrated while immersed in a bath. The customary melting-point apparatus has only a portion of the stem immersed. The mercury thread above this point has a temperature lower than that at which the thermometer was calibrated. Hence a correction must be applied to allow for the difference in length of the column of mercury which is above the bath. This correction is made by the relation

$$\text{Stem correction} = \underline{Kn}(T^{\circ} - t^{\circ})$$

where K refers to the differential expansion coefficient of mercury in glass, n designates the number of degrees emergent from the bath, T° the bath temperature, and t° the mean temperature of the emergent stem (determined by an auxiliary thermometer). The value³⁶ of K on the centigrade scale for normal glass is 0.000158 from 0 to 150°; 0.000159 at 200°; 0.000161 at 250°; and 0.000164 at 300°. For borosilicate glass the values for different temperatures are 100°, 0.000164; 150°, 0.000165; 200°, 0.000167; 250°, 0.000170; 300°, 0.000174; 350°, 0.000178; 400°, 0.000183; 450°, 0.000188. The average temperature of the exposed stem is read on an auxiliary thermometer placed alongside with its bulb at the middle of the exposed mercury thread.

Partial-immersion thermometers are calibrated under the same conditions to which they will be subjected in the melting-point apparatus, making a stem correction theoretically unnecessary. Such direct-reading thermometers have a clearly marked immersion line, usually 8 cm. above the bulb. In actual use they should be immersed to this same depth. Waidner and Mueller,³⁷ in comparing these thermometers with those of the total-immersion type, found that the former are subject to variations in readings if the exposed-stem temperatures are different from those at which calibrations were made, such as might happen, for example, if the top of the apparatus were enclosed instead of open. A total-immersion thermometer is generally more accurate if the correction is carefully determined, but such accuracy is not always possible with an auxiliary thermometer hung beside the stem. Accurate stem correction can be had only with a special capillary thermometer—one with a long capillary bulb for measuring the average temperature of the portion of the stem beside

it—such as is rarely used outside a thermometer standardizing outfit. At 300°, with a partial-immersion thermometer, the average maximum error would be only about 1° and would probably never exceed 2.4°. For the total-immersion type at 300° and an average exposed stem temperature of 40°, the correction would be $0.00016 \times 300 (300 - 40) = 12.5^\circ$, which can be determined to an accuracy of 0.5° provided the stem temperature is correct to 10°. Below 300° the results with the partially immersed type are less accurate because of differences in the temperature of the laboratory at different seasons. The probable error at 90° (with 90° of emergent stem) is estimated at 0.2°, whereas with total immersion the maximum error is estimated at 0.1° even when the average temperature of the emergent stem is determined by an ordinary thermometer. All of the foregoing applies to thermometers graduated in 1 or 2° intervals. Thermometers with graduations in smaller divisions, *e.g.*, in 0.1 or 0.2°, will not usually give better results unless graduated and used under conditions of total immersion or with accurate determination of exposed-stem temperature. Otherwise the benefits from finer division are lost. Thermometers graduated in intervals smaller than 0.5° should not, in general, be graduated as partial-immersion thermometers if the accuracy of which they are capable is desired, unless such fine graduations are of importance for other reasons.

45. *Calibration of the thermometer* can be carried out very conveniently by comparing its readings with correct values at the freezing or boiling points of reference compounds. The zero reading is best obtained by immersion in a slush of ice and water; that at 100°, by suspension in the vapor of boiling water. Variations of pressure in the neighborhood of 760 mm. can be corrected for by the relation 1 mm. = 0.0367°. For a 1° variation from the 100° point the error due to the use of this figure over what would be obtained by reference to steam tables is less than 0.02°, a value well within the limit of error of ordinary use of a melting-point thermometer. Great care must be exercised with regard to making appropriate stem corrections³⁸ if the thermometer is not totally immersed in the vapor. Timmermans and Martin³⁹ give a list of liquids that can be used for calibration at the boiling point (see Table 16). Changes in temperature for

every 10 mm. of mercury pressure change in the vicinity of 760 mm. are given in the last column.

TABLE 16.—COMPOUNDS FOR CALIBRATION OF THERMOMETERS

Compound	Boiling point, °C.	$dt/10$ mm., °C.
Isopentane.....	27.95	0.37
Carbon disulfide.....	46.25	0.42
Chloroform.....	61.20	0.38
Benzene.....	80.20	0.43
Water.....	100.00	0.37
Toluene.....	110.80	0.42
Chlorobenzene.....	132.0	0.49
Bromobenzene.....	156.15	0.53
Aniline.....	184.4	0.51
Nitrobenzene.....	210.85	0.48
Naphthalene.....	218.0	0.58

For temperatures higher than 218° the boiling points of benzo-phenone (305.9°) and sulfur (444.6°) may be used.

46. Micro Methods.—With the increasing importance of micro chemistry it is not surprising that the advantages⁴⁰ offered by use of a microscope have been adapted to melting-point determinations. The behavior of individual crystals on melting can be followed closely and can frequently be utilized in forming an opinion of their purity. If crystals are anisotropic, the disappearance on melting of brilliant polarization colors under polarized light is especially helpful. Changes in crystal form, decomposition temperatures, and presence of water of crystallization can be clearly observed. If, as is usually the case, a cover glass is over the crystals, the tendency to sublime and the state of dryness of a sample can be judged by the appearance of a deposit on the underside of the glass. Mixed melting points are easily and accurately determined. All of the foregoing advantages have prompted a variety of apparatus so that it is now possible to determine the melting point with as much accuracy as is possible with the average good apparatus commonly used with larger samples.

47. Apparatus varies considerably, but an essential part is a metal plate approximately 60 to 85 mm. in diameter (rectangu-

lar dimensions may be used if desired) and 15 to 20 mm. thick. It is heated by suitably insulated electrical wires which circle the block or, in the case of the rectangular form of Amdur and Hjort,⁴¹ pass through it. A hole 1.5 to 3 mm. in diameter is drilled vertically through the center, so that the usual lighting necessary with a microscope can be used, and is enlarged at one end to admit a thin cover glass on which the sample is placed. It is shielded from cooling air currents above by a glass plate and below by glass or mica. The temperature of the block is kept uniform by asbestos boards on top and bottom. Measurements are made with a thermocouple or thermometer placed in a well as close as possible to the sample. The whole apparatus rests on insulated legs on the microscope stand. Special attention is usually directed to insuring accurate temperature measurements so that corrections are unnecessary. The chief difficulty arises from cooling air currents and a lag in heat transfer through the thin cover glass on which the sample rests. In the better types of apparatus it is now possible to obtain measurements that require no correction. Only a few types can be described in detail.

Kofler and Hilbeck⁴² use a metal box 85 mm. in diameter by 15 mm. high inside which are placed heating coils. In the center of the top and bottom of this box are glass windows 3 to 7 mm. in diameter. On the underside are three insulated legs to support the apparatus on the microscope. On the upper side, held in place by clamps, is a nickel-plated removable copper plate 2.5 mm. thick, with a central opening 1.5 mm. in diameter. Temperatures on the surface are measured by a copper-constantan element, located approximately 20 to 25 mm. from the central opening, whose wires for about 70 to 80 mm. of their length are fastened by small screws (the copper wires directly and the constantan through thin mica) to the copper plate in order to avoid any error through loss of heat from the soldered to the cold parts of the wire. As a shield against air currents, a removable metal ring, insulated by asbestos, rests on four projections from the sides of the hotbox and supports a removable glass plate about 6 mm. above the nickel-plated block. The crystal is placed on a slide in the middle of the copper plate over the small opening and is then covered with a cover glass. The shield is set in

place, and the melting point determined. An enlargement of one hundred thirty-five times (sixty is more common) may be used with this apparatus. Temperatures as high as the melting point of anthraquinone (284.5 to 285.5°) have been measured. Kofler⁴³ subsequently modified his apparatus so that a thermometer could be used. The new apparatus consists of an electrically heated metal hot plate through the middle of which is a 1.5-mm. opening for light. It is shielded from air currents by a ring, extending 6 mm. above the surface and supporting a glass plate whose edges are ground to fit tightly. The thermometer is inserted in an opening in the side and is protected against breakage by an open metal case screwed to the hot plate.

To insure better heat transfer Burt-Gerrans⁴⁴ eliminated the air space under the cover glass and used reflected light from a vertical illuminator such as is used for mineralogical or other solid specimens. A silver disk (silver because of its good thermal conductance) 60 mm. in diameter and 25 mm. thick is provided on its upper side with a shallow circular machined depression large enough to hold a small cover glass on which crystals lie. A larger cover glass protects this opening from air currents. Resistance wire is wound about the disk; a hole for a thermocouple is made so that it terminates directly beneath the central depression; and the block is well lagged with asbestos board to prevent heat losses. Very close agreement with the values obtained in a conventional melting-point apparatus is claimed.

Schürhoff⁴⁵ constructed a very simple apparatus which consists of an asbestos board 9 by 13 cm. with a 1.5-cm. opening in the middle, a copper plate 7 by 19 cm. with a 1-cm. opening 5 cm. from one end so that the portion that projects beyond the asbestos can be heated with a gas flame, and above this a flat flask 1.5 cm. thick and 6 cm. in diameter with a 1.3-cm. neck 6 cm. long supported at an angle of 45 deg. from the flask. A thermometer can be inserted in this neck so that its bulb is in the flask. The sample is placed on the flat surface, covered with a cover glass, and this, in turn, covered by an inverted watch glass. Paraffin or other transparent oil is used as the bath liquid in the flask. When the temperature is within 10 to 15° of the melting point the flame is reduced so that a slow rise to the melting point is insured.

Many other pieces⁴⁶ of apparatus have been described which make use of a microscope in melting-point determinations. Attention might also be directed again to the use of Walsh's³² apparatus (Sec. 42) with which the melting point of a single crystal in a capillary can be determined.

48. The Curve Method. *The Time-temperature Cooling Curve.* An accurate and precise method of determining melting point is by use of a cooling curve.⁴⁷ Not only does it recognize absolute purity when reached, but it also provides knowledge of the per-

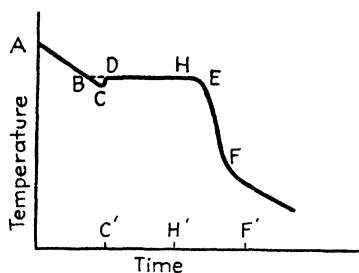


FIG. 14.—Time-temperature cooling curve.

centage impurity and the correct melting point. Means by which such information is obtained is indeed simple. In a suitable apparatus, such as will be described later, the time-temperature data for solidification of a melt are obtained and then plotted as illustrated in Fig. 14.

The line A, B, C, D, E, F, represents the course of the change from the liquid state, through supercooling and freezing, to the completely solid condition.

Let us suppose that 1 per cent of an impurity is present. Solidification begins at C (at B in the limiting case of no supercooling) and is completed at F. The time required for this change to occur is represented on the abscissas by the distance C' to F'. At half time H' half of the solvent has crystallized out of the melt. If the solution is perfect, the impurity has not solidified but has remained in the melt. Hence the amount of foreign material originally present as 1 per cent is now in solution as 2 per cent in the remaining mother liquor. In accordance with Raoult's law the depression of the freezing point at the half period of solidification will be twice as great as it was at the beginning of the operation. Expressed in another manner, the temperature of the melt at point H will be as much below the initial freezing point T_i of the compound as the latter is below the correct melting point T , for the pure compound. It is obvious from the foregoing that the correct melting point may be determined by noting the temperature at start and mid-point of

freezing and then adding the difference between the two values to the initial observation.

The theory on which this method is based is essentially the same as that on which determinations of molecular weight by freezing-point depression are made. The mixture is assumed to be a perfect solution in which the impurity is the solute. The depression of the freezing point of the material, which serves as the solvent, will then be expressed by Raoult's law. But whereas in molecular-weight determination we increase the concentration of solute by direct addition of a pellet of solid or of drops of liquid, in this method we make an increase by abstraction of half of the solvent by the device of crystallization. This manner of halving the quantity of solvent is justified if the solution is a perfect one, for in that case pure solvent only will crystallize from solution. The concentration of impurity having been doubled by this means, the depression of the freezing point at T_h will now be twice as great as the original depression at T_i . The freezing point T_c in the absence of all impurity will therefore be obtained by the relationship $T_c = T_i + (T_i - T_h)$. The assumption is made that heat is abstracted at a uniform rate. With ordinary precautions and within the temperature range concerned, this assumption will be approximately correct.

It is now apparent that the same principle can be used to *estimate percentage impurity*. The value of K for the molecular freezing-point depression in 100 g. of solvent either is known or can be approximated by addition of a known substance. From this value of K and the depression $T_c - T_i$ the number of moles n of impurity in a weight of sample W may be calculated by the expression $n = \frac{(T_c - T_i)}{K} \frac{W}{100}$. The mol percentage impurity may thus be obtained exactly. The weight percentage purity can be determined only if the nature of the impurity is known or can be safely estimated. An attractive feature of the curve method is that estimation of amount of impurity is independent of the nature or accuracy of the thermometer. Purity is judged by the curve's flatness for the first half of the freezing period and requires no calibrated thermometer. Neither is the observation dependent upon rate of heating. Moreover, purity is recognized as soon as it is reached without the necessity of an

additional crystallization as in the case of the capillary-tube method. It may be argued that the curve method will not apply to those cases where mixed melting points seemingly show no depression. It should be remembered that with these mixtures a cooling curve reveals a deviation from flatness over the first half of the freezing period, as contrasted with the observation of initial freezing point which is merely one value on the whole curve. The curve method may be inapplicable to some mixtures⁴⁸ of *d* and *l* isomers in which the melting points of the two forms are the same and mixed crystals form on cooling. Thus, each *d* and *l* pair of camphene, bornyl hydrogen phthalate,

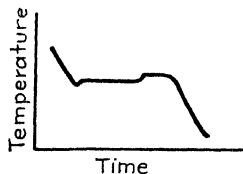


FIG. 15.—Shape of cooling curve of a compound with two melting points.

camphoric anhydride, and camphor have very similar, if not identical, melting points and form mixed crystals of the same melting point. On the other hand, the presence of the *l* form of pinene will lower the melting point of its *d* isomer in the same manner that any other foreign substance will act on a perfect solution. The *d* and *l* forms of camphoric acid not only depress

the freezing points when either is present in small quantity in the other but also form a racemic compound of higher melting point. The curve method is inapplicable to eutectic mixtures, but the chance of meeting a mixture of such definite proportions in ordinary laboratory work is in truth unlikely. Some difficulties are encountered with substances that crystallize in two different forms. Ortho nitrobenzaldehyde,⁴⁹ for example, exists in two modifications, a β unstable one which melts at 37.9° and an α stable variety which melts at 40.9°. The curve (Fig. 15) shows a halt of 12 min. duration for the lower form, followed by a rise in temperature as the change to the higher melting form occurs. All of these possible exceptions show the care that must be exercised in using the cooling curve as a sole criterion of absolute purity. Usually, other facts relating to the source or nature of the compound aid⁵⁰ in arriving at a definite conclusion. In general, the curve method is capable of wide applicability. The main disadvantage is the apparatus and quantity of material as compared with that required in a capillary tube. As will be shown later, this objection is not a serious handicap, particularly

when weighed against assurance of more accurate information about purity.

49. The Heating Curve.—Instead of a cooling curve, the heating curve⁵¹ of a compound may be measured. This procedure offers the advantages that no necessity exists for inoculating and stirring and no difficulty is found with compounds that fail to crystallize. Substances that have two different modifications are observed more easily. There is an interesting difference in interpretation of cooling and heating curves. In the former all major observations are at the beginning, and the drop at the end of freezing is difficult to interpret. It is upon this very end that critical observations of the heating curve are made. As bath and shield temperatures are raised, those of the compound parallel the rise until the melting point is approached. The sharpness of the break from the normal curve at this point is an indication of the compound's purity. A correct melting point is, however, determined less easily by the heating curve. No doubt the greater homogeneity which exists when crystallizing from a melt favors a true equilibrium condition at the beginning of crystallization.

50. Apparatus and Manipulation.—*The essential parts of any apparatus* used for the curve method are a bath of sufficient size to permit cooling at a controlled rate; a stirrer to insure evenness of temperature in the bath; a tube, which is usually air-jacketed by insertion in a larger tube, to serve as a container for the compound; and a thermometer or thermocouple, located centrally in the melt, for measuring temperature. The particular construction depends to a large extent on the sample's size. Obviously the smaller the quantity of material the greater must be the care taken to control the cooling rate. Regardless of the type of apparatus used, the amount of supercooling must be reduced to a minimum if correct temperatures are to be had*. In fact, the results may be valueless, even with a pure compound, if super-

* This statement must be accepted with some caution. Skau⁵¹ maintains that a certain amount of supercooling is necessary. He has pointed out that in the absence of stirring, part of the sample on the outside wall freezes and forms an outer shell about the remaining melt. This shell then becomes cooled further so that nonequilibrium conditions are set up in the sample causing erratic results. If supercooling is adequate a network of crystals are set up through the material so that segregation on the sides, top, or

cooling is too great. A novel method⁵² of seeding to induce crystallization from the supercooled state is to wet a glass bead with the solvent, place it in a small dry test tube, chill it in a freezing mixture, and then roll the crystal-coated bead into the supercooled system. Liquids or solutions that have been supercooled only 0.04° have been induced to crystallize by this method. Where the container is too small to admit a glass bead satisfactorily, a useful method⁵³ is to allow the hammer of an electric bell to vibrate against the side of the tube or thermometer either one of which must be hung loosely from the top so that vibrations will not be damped. In lieu of an electric-bell tapper a stiff piece of cardboard⁵⁴ may be mounted on a motor stirrer so that it strikes and vibrates the tube while being rapidly rotated. These last two devices are valuable for maintaining equilibrium conditions, since stirring of the melt is impossible after approximately 25 per cent has solidified.

It is difficult to know exactly when the *end of freezing* has been reached. In an ideal case the temperature of the solidified melt should resume a downward slope approximately parallel to that of the bath. In actual practice this break is never sharp even when the compound is reasonably pure and is exceedingly difficult to estimate when the substance is very impure. Constant agitation with the electric-bell hammer helps considerably in maintaining equilibrium conditions at this end of the curve and hence improves the sharpness of the break. Empirically the end of freezing can be taken at a point on the downward vertical line. In cases of doubtful purity or of sufficient importance a comparison curve with a sample containing a known percentage of impurity enhances the value of information obtained in these measurements.

51. Some specific illustrations of apparatus are given to show the great variety possible. A *simple apparatus*, originally used⁵⁵ for observing the cooling curve of camphor, is made from a beaker wrapped with asbestos and set on a bed of sand in a tin can. Glycerol (about 400 ml.), which is used as the bath liquid, is stirred mechanically. The camphor, 0.3 to 0.7 g., is put into a small test tube (10 by 60 mm.); the cork carrying the thermometer is

bottom is avoided. Adequate stirring or agitation should do much to remedy this trouble.

inserted; and the tube is immersed in the bath up to 2 to 3 mm. from the bottom of the cork. The bath is first heated to about 180°C . with a Méker burner, after which the rate of cooling is adjusted to 0.4 to 0.8° a minute by regulating a Bunsen flame. This apparatus was used for molecular-weight determinations of substances so difficultly soluble that the full curve had to be known in order to observe the depression.

Dewar test tubes, containing a depression at the bottom^{56,57} (Fig. 16) for holding the material, have been found satisfactory. When the tube is constructed from pyrex glass it can withstand temperatures as high as 500°C . No stem corrections are usually necessary, because the walls of the tube are substantially at the same temperature as the melt. For extreme high or low temperatures an extra thermometer may be inserted next to the stem. The Dewar tube with its loosely fitting stopper and thermometer is first heated in a hot oven to a temperature somewhat above the melting point of the sample. The melted sample is then poured into the tube, the thermometer or thermocouple inserted, and the time-temperature readings recorded. The thermometer should be tapped at regular intervals. Seeding crystals or other devices may be employed to overcome excessive supercooling. For substances that melt below room temperature a heating curve is better. The Dewar tube, cork, and thermometer are cooled to a temperature below the melting point of the compound, after which crystals of the substance are added, and the mass stirred with the thermometer. Time-temperature readings are made as before, and the data plotted to determine the melting point. The apparatus is very useful, especially when in the convenient small test tube size.

Electrical heat⁵⁸ can be applied conveniently inside a small Dewar tube as illustrated in Fig. 17. The sample is contained in a small thin-walled test tube which fits fairly closely into another pyrex tube wound externally with fine nichrome wire. This tube, in turn, is set inside a small unsilvered Dewar tube 12 mm. inside diameter and 20 cm. long. Heating or cooling rates can

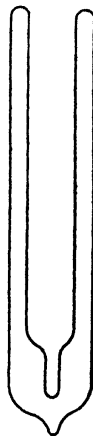


FIG. 16.—
Dewar test
tube, Wash-
burn and
Read type,
for observing
the cooling
curve.

be adjusted by a rheostat in series with the heater. The thermometer or thermoelement, previously calibrated in the apparatus by a series of known melting temperatures, should be embedded centrally, using lugs if necessary, in the small test tube.

Suitable cooling curves may be obtained on 0.5 to 1.0 g. of material.

A silvered Dewar tube containing paraffin as the bath liquid, or hot air if the temperature is above 100° , is described by Andrews, Kohman, and Johnston,⁴⁷ and a modification of this apparatus, using a copper block as a bath, was used by Skau and Saxton.⁵⁹ The metal is set upon asbestos at the bottom of the Dewar tube, is heated by resistance wire wrapped tightly about mica insulation, and is bored with wells for thermometer and vacuum-jacketed sample tube. White⁴⁷ achieved a uniform thermal environment without a Dewar flask by means of a liquid bath and air-jacketed container.

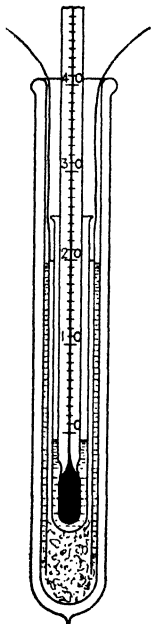


Fig. 17.—
Small Dewar
tube with internal
heater as
used by Johnston
in observing
the cooling
curve.

Control of the rate of cooling can be secured by *varying the pressure in a double-walled tube*. In determining the cooling curve for hexane, octane, decane, and dodecane⁶⁰ the sample was placed in this tube, which, in turn, was fitted into a brass tube as a safety precaution and immersed in liquid air. By varying the exhaustion in the annular space the cooling could be adjusted to the desired rate. For very low melting compounds large samples give more accurate results. With pentane,⁶¹ observations were made on 120-ml. portions; with butene-2,⁶² more reliable results were obtained with 40 than with 1 ml. In the last-named work a magnetically operated stirrer was employed. An additional check on purity was obtained by making a final determination with 0.5 per cent of added impurity and noting the change in the shape of the curve.

MISCELLANEOUS METHODS

52. The Maquenne block⁶³ consists of a rectangular brass block on the surface of which are a number of small depressions located

in a line directly above a long horizontal opening in which a thermometer can be placed. The block is heated by several gas burners, and the sample is placed in the depression which will permit the stem of the thermometer to be inserted far enough to avoid the necessity of any stem correction. The sample should be covered by a small cover glass, particularly if it sublimes. *Dennis and Shelton*¹⁶ employed a long *copper bar*, 24 by 1 by 1 in., heated electrically at one end. When the bar reaches thermal equilibrium, crystals are spread along the surface; the line where they just melt is observed; and a constantan point is pressed against the copper bar at this juncture to complete the electrical circuit of a thermoelement. Determinations may be made very rapidly. The apparatus is convenient when a large number of determinations within a range of 100° are to be made and is particularly valuable with compounds that decompose on melting. Mention might also be made of the novel *apparatus of Dubosc*,⁶⁴ who coated two small platinum spheres by immersion in the melted sample. The terminals of the platinum wires were connected to a source of current through an electric bell, and the spheres, insulated by films of solid organic matter on their surfaces, were immersed in a mercury bath on either side of a thermometer. When the melting point was reached, the insulation around the points was melted; the current flowed; and the bell rang as a signal to read the thermometer. Such an apparatus had possibilities⁶⁵ of an automatic nature too great to be overlooked. A maximum thermometer, reading to 250°, was inserted in the bath with the requisite number of pulleys, and so forth, to lift the thermometer out when the bell rang. The operator could thus attend to reading the temperature at his leisure. The melting points of *p*-dichlorobenzene, acetanilide, and salicylic acid are reported as agreeing with 0.1 to 0.4° of the values found by the capillary-tube method. Another automatic device for use with the capillary-tube method is described by Wick and Barchfeld.⁶⁶ A very thin glass rod, resting on the sample in the tube, supports a metal contact which closes the circuit when the sample melts, permitting the rod to fall. Their determinations were made in the copper block. For methods of determining the melting points of asphalt and resins, the reader is referred to specifications given by the American Society of Testing Materials.⁶⁷

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CHAPTER III

THE BOILING POINT

53. An organic compound may be characterized by its boiling point. Since this value is not a triple-point equilibrium, as in the case of the melting point, it varies with pressure. For the most part, boiling points recorded in the literature are observed with the thermometer in the vapor phase, a method that is generally

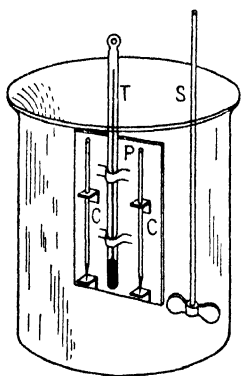


FIG. 18.—Micro boiling-point apparatus of Emich, showing *S*, stirrer; *T*, thermometer; *P*, metal plate; and *C*, capillary tubes supported in sections of the plate bent at right angles to the metal.

satisfactory. Strictly speaking, however, the boiling point of a liquid is that which is observed when the thermometer is in contact with both liquid and vapor phases so that the temperature is observed under equilibrium conditions. In short, the boiling temperature is not that at the top of the fractionating column but that in the liquid itself with suitable provision against errors which arise from superheating. Some of the discussion in this chapter is from this point of view. The important use of the boiling point as a criterion of purity or identity of a material is also described.

54. Micro Methods.—In the *procedure of Emich*¹ a single drop is touched with a very fine capillary, open at both ends, so that a portion rises in the tube by capillary attraction. The tube is then sealed at the tip nearest the liquid by touching it in a micro flame. In this way a minute bubble of air, which prevents superheating of the liquid during the determination, is entrapped. Care must be taken lest this bubble be too large, for excessive size is one of the most common sources of error. If the end of the capillary which holds the liquid has previously been carefully tapered to a fine point, the droplet will have a tendency to stay near the end and the trapped bubble will

be smaller. The tube is then attached to a thermometer with the holder usually employed in melting-point determinations or is preferably supported on a thin metal plate (the supports can be made by cutting two 5- by 5-mm. slits and bending them at right angles to the plate, the upper with a hole and the lower with a small depression) which, in turn, can be fastened to the thermometer. Heat is applied slowly and regularly from a glycerol or oil bath (Fig. 18) equipped with a stirrer; the drop rises in the tube and just passes the surface of the bath at the boiling point.

*Siwoloboff's*² method is to place a few drops of the liquid in a capillary tube and insert a smaller capillary, open end downward, into the liquid. The tube is then attached to a thermometer (Fig. 19) and heated in any conventional melting-point apparatus until a continuous stream of bubbles emerges from the tube.

The first apparatus for micro boiling-point determination was that of Jones³ who in principle inserted the sample in the closed arm of a U-type manometer and heated it in a bath until the vapor pressure of the sample in the closed arm was exactly balanced by that of air. Subsequently this apparatus was modified by Schleiermacher⁴ and by Arrequine.⁵

When a minute amount of liquid, adsorbed on a piece of warm tile which has been previously ignited, is heated over mercury in a flask of approximately 10-ml. capacity closed with a capillary (see Fig. 20), the metal is expelled through the tube at an accelerated rate when the boiling point is reached. With appropriate corrections for added pressure of mercury, this method, in the hands of *Niederl and Routh*,⁶ has been successfully utilized for boiling-point determinations. By adsorbing the drop on a piece of tile the difficulties inherent in introducing a liquid sample into the closed section over mercury are largely eliminated. Care must be taken to expel all bubbles of air from the mercury.

55. Macro Methods.—Apparatus for determining boiling points of larger quantities of material is essentially the same as that for molecular-weight determinations. Because of its impor-



FIG. 19.—*Siwoloboff* micro boiling-point tube. Drawing shows capillary tube containing another inverted capillary.

tance for testing purity and identity, however, it is proper to cover this subject rather carefully. A common apparatus (see Fig. 21) is that of *Washburn and Read*,⁷ as modified by *Spencer*,⁸

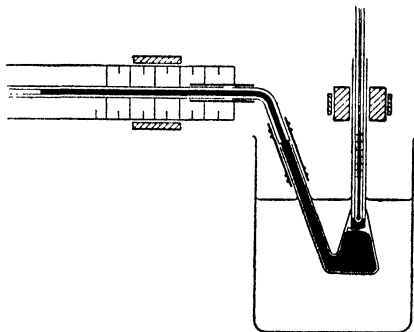


FIG. 20.—Micro boiling-point apparatus of Niederl and Routh.

which utilizes the Cottrell⁹ pump. The latter is an inverted funnel with beads on its rim to lift it slightly off the bottom of the flask in which it sits and with its stem divided into three prongs so as to encase the bulb of a Beckmann thermometer. When heat is applied directly beneath the funnel, boiling liquid is forced upward and out through holes in the prongs so that it impinges on the thermometer bulb. Erroneous results which might arise with insertion of thermometer in the liquid are thus avoided, and equilibrium conditions between vapor and boiling liquid are rapidly attained.

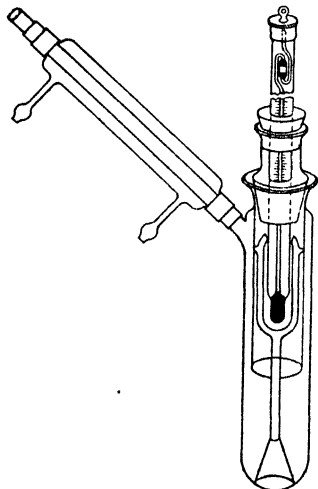


FIG. 21.—Boiling-point apparatus of Washburn and Read.

Davis'¹⁰ apparatus (Fig. 22) is simple in design and exceedingly satisfactory. The Cottrell pump is made large enough to insure that all boiling occurs under the funnel. In operation it is filled to about the level of the return spout below the thermometer. A short piece of platinum wire, sealed in the bottom, insures regular and smooth ebullition.

The *ebullioscope of Swietoslawski*¹¹ is a Cottrell pump made into a flask. The simplest form, shown in Fig. 23, illustrates how a mass of liquid and vapor is forced over the thermometer bulb when the flask is heated. A more complicated apparatus is pictured in Fig. 24. Two thermometers, whose bulbs are enclosed in glass wells filled with mercury, record vapor and liquid temperatures simultaneously. To insure even boiling, the interior surface of the flask is roughened by adding a dilute solution of sodium silicate, evaporating the water, and heating to a dull-red

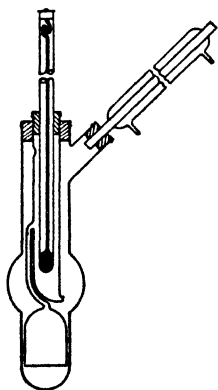


FIG. 22.—Davis apparatus for determining boiling points.

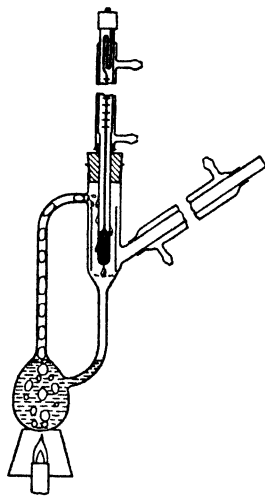


FIG. 23.—Swietoslawski apparatus for determination of the boiling point.

heat. After cooling it is washed with dilute hydrochloric acid, boiled with distilled water, and dried. Powdered glass may also be sintered into the bottom of the flask. Addition of iron powder is helpful at times. Glass spirals, encircling the thermometer cups, keep the liquid in contact with the glass for a longer time. Operation is relatively simple. A measured volume of solvent, sufficient to more than fill the flask, is introduced through the side arm. Heat is applied from either a resistance coil or a gas burner. In the latter case a wire gauze should be wrapped about the bottom of the flask. This apparatus can be made in a number of different sizes. Swietoslawski describes one which has a

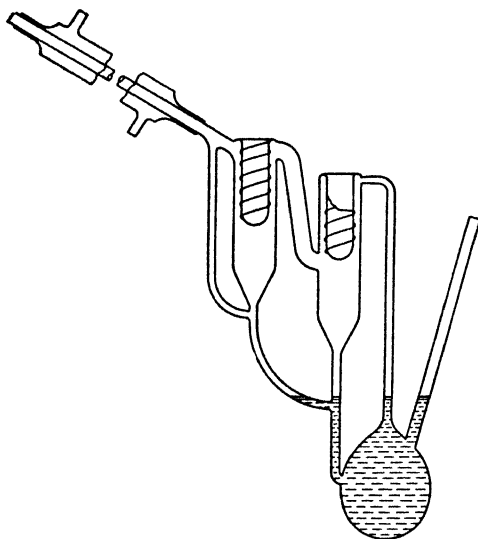


FIG. 24.—Swietoslawski's apparatus for simultaneous determination of liquid and vapor temperatures.

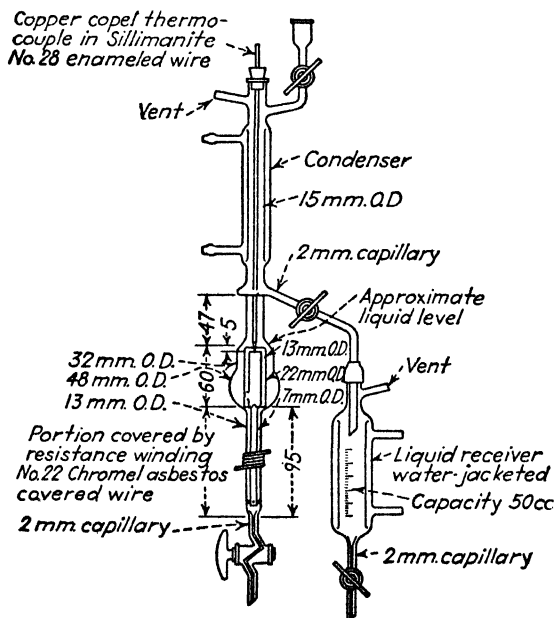


FIG. 25.—Boiling-point apparatus of Quiggle, Fenske, and Tongberg in which continuous removal of sample is possible.

capacity of 200 ml., and in the author's laboratory one for 5 ml. of liquid has worked satisfactorily.

Samples may be drawn off at will in the apparatus of *Quiggle, Fenske, and Tongberg*¹² (see Fig. 25) so that the boiling-point range can be determined accurately. A coil heater around the stem pumps liquid through the annular space between two inner tubes over the thermocouple and back through the innermost tube. This inner assembly is centered at the bottom by glass lugs and at the top by indentations in the outer shell. From a 50-ml. charge, 70 to 75 per cent can be distilled before liquid ceases to impinge on the thermocouple. Determinations of the boiling point can be made with as little as 5 to 10 ml. of material. Willard and Crabtree¹³ have constructed an apparatus one-tenth the size on similar lines for use on a semi-micro scale.

56. Thermometers.—Apart from the ordinary laboratory thermometers, special ones are necessary for measuring small differences in temperature. We are indebted to *Beckmann*¹⁴ for one of the most common forms, which makes use of the expansion of mercury from a large bulb into a small capillary (see Fig. 26). Owing to the small temperature range (4 to 6°) of the stem, a reservoir is provided at the top, from or to which transfer of metal is made until the end of the capillary thread is on the scale at the desired working temperature. This exchange of mercury is accomplished easily by inserting the bulb in a hot bath until the liquid rises through the capillary and makes contact with the reservoir, cooling or further heating and then breaking the thread with a sharp rap when proper transfer has been made. When making temperature readings the thermometer should be tapped to prevent sticking of metal to the capillary wall.

57. The Differential Thermometer.—This apparatus (see Fig. 27), as developed by *Menzies*,¹⁵ makes use of differences in vapor pressure of water, enclosed in a small evacuated tube,

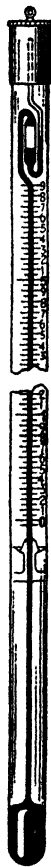


FIG. 26.—
Beckmann
thermometer.

between the temperatures of a boiling solution and its vapor. The lower bulb is wet by the spill from a Cottrell pump; upper bulb and stem, by the vapors which pass upward and the hot condensate which drains back on the two guide wires. In molecular-weight determinations the temperature of the vapor is constant, while that of the solvent is dependent on the concentration of solute. Hence pressure changes in the bulb, arising from varying solution strength, cause differences in the heights

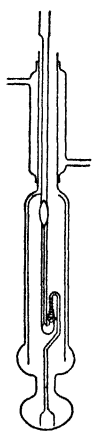


FIG. 27.—
Differential
thermometer
and boiling-
point appara-
tus of Men-
zies.

to which water is forced up in the large capillary. The amount of this rise, which corresponds to a centigrade degree, varies with the temperature at which the observation is made, but in any event the sensitivity is ten to fifty times greater than that possible with a Beckmann thermometer. Table 17 gives the change in temperature corresponding to a vapor-pressure change of water equal to 1 mm. difference in the height of water in the stem above the bulb. Levels in both stem and bulb must, of course, be read in making observations, but the relationships between bulb and stem heights may be determined once for all and put upon a graph. Substances other than water may be used as the thermometer liquid, particularly if the boiling point of the solution is high.

Menzies used in his apparatus a set of constants slightly different (see Table 19) from those which are used with the Beckmann thermometer, because the working volume, *i.e.*, the original volume less that of pure solvent which is washing down the walls of the apparatus, is made the basis for calculation. This working volume is found by boiling the pure liquid until readings are constant, removing the flame, and reading the volume in the graduated neck as soon as ebullition has ceased.

Operations are very simple. An ordinary mercury thermometer is first hung in the vapor, and the boiling point of the solvent determined, a procedure seen to be an obvious necessity by reference to the different values in Table 17 for the conversion of millimeters of water into centigrade degrees at different temperatures. The thermometer is next removed, and the working

TABLE 17

Against each tenth of a degree from 33.0 to 101.9° is entered the change of temperature in degrees centigrade that would correspond to a vapor-pressure change of water of 1-mm. head of water at the same temperature.

°C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Diff.
33	0 03449	3433	3417	3400	3384	3367	3351	3334	3317	3301	16
34	0 03286	3270	3254	3238	3222	3207	3192	3177	3161	3146	16
35	0 03130	3116	3101	3086	3071	3056	3041	3026	3011	2997	15
36	0 02984	2969	2955	2941	2927	2913	2899	2885	2872	2858	14
37	0 02844	2831	2818	2805	2791	2778	2765	2751	2738	2726	13
38	0 02713	2700	2687	2675	2663	2650	2637	2625	2613	2600	12
39	0 02588	2576	2564	2552	2540	2528	2517	2505	2494	2482	12
40	0 02471	2459	2447	2436	2425	2414	2403	2392	2381	2370	11
41	0 02359	2348	2338	2328	2317	2307	2296	2285	2275	2264	11
42	0 02254	2244	2233	2223	2213	2203	2193	2183	2173	2163	10
43	0 02154	2144	2134	2124	2114	2105	2096	2086	2077	2068	10
44	0 02059	2049	2040	2031	2022	2013	2004	1995	1986	1977	9
45	0 01969	1960	1951	1943	1934	1926	1917	1908	1900	1891	9
46	0 01883	1875	1866	1858	1850	1842	1834	1826	1818	1810	8
47	0 01802	1794	1786	1778	1770	1763	1755	1748	1740	1732	8
48	0 01725	1717	1710	1702	1694	1687	1680	1673	1665	1658	7
49	0 01651	1644	1637	1630	1623	1616	1609	1602	1595	1588	7
50	0 01581	1575	1568	1561	1554	1548	1542	1535	1529	1522	7
51	0 01516	1510	1503	1496	1490	1484	1478	1472	1466	1459	6
52	0 01453	1447	1441	1435	1429	1423	1417	1411	1405	1399	6
53	0 01393	1388	1382	1376	1370	1364	1358	1353	1348	1342	6
54	0 01336	1330	1325	1319	1314	1308	1303	1298	1292	1287	6
55	0 01281	1276	1271	1266	1261	1255	1250	1245	1240	1235	5
56	0 01230	1225	1220	1215	1210	1205	1200	1195	1190	1185	5
57	0 01180	1175	1170	1166	1161	1156	1152	1148	1143	1138	5
58	0 01133	1128	1124	1119	1115	1110	1106	1102	1097	1092	4
59	0 01087	1083	1079	1075	1071	1067	1063	1058	1054	1049	4
60	0 01045	1041	1037	1033	1029	1025	1021	1017	1013	1009	4
61	0 01005	1001	9968	9928	9890	9851	9813	9772	9734	9696	
62	0 009658	9620	9583	9545	9508	9470	9432	9396	9359	9322	37
63	0 009285	9249	9212	9177	9141	9105	9069	9034	8999	8963	35
64	0 008931	8896	8861	8826	8792	8758	8725	8692	8658	8624	34
65	0 008592	8559	8527	8494	8461	8428	8397	8365	8333	8301	32
66	0 008269	8237	8207	8175	8145	8114	8083	8052	8022	7991	31
67	0 007960	7930	7900	7870	7840	7810	7780	7750	7721	7691	30
68	0 007663	7633	7605	7575	7548	7519	7491	7463	7435	7406	29
69	0 007379	7352	7324	7297	7269	7242	7214	7188	7161	7135	27
70	0 007109	7083	7057	7031	7005	6979	6953	6928	6902	6877	26
71	0 006852	6826	6801	6776	6751	6727	6702	6677	6653	6629	25
72	0 006606	6582	6557	6533	6509	6485	6462	6439	6415	6392	24
73	0 006369	6346	6323	6301	6277	6255	6232	6210	6187	6165	23
74	0 006144	6121	6099	6077	6055	6033	6011	5989	5969	5947	22
75	0 005927	5906	5884	5863	5842	5822	5801	5781	5760	5740	21
76	0 005719	5698	5676	5657	5637	5618	5598	5578	5558	5539	20
77	0 005520	5499	5480	5461	5442	5423	5404	5384	5365	5347	19
78	0 005328	5310	5291	5273	5254	5236	5218	5200	5182	5163	18
79	0 005145	5127	5109	5091	5074	5056	5039	5021	5003	4986	18
80	0 004969	4952	4935	4918	4901	4884	4867	4851	4834	4817	17
81	0 004800	4784	4767	4751	4735	4719	4702	4686	4670	4654	16
82	0 004638	4623	4607	4592	4576	4560	4545	4530	4514	4499	15
83	0 004484	4469	4453	4438	4423	4408	4393	4378	4363	4349	15
84	0 004334	4319	4305	4290	4276	4262	4248	4234	4220	4206	14
85	0 004192	4178	4165	4151	4137	4124	4111	4097	4083	4069	14
86	0 004055	4042	4029	4016	4002	3989	3976	3963	3950	3937	13
87	0 003923	3910	3897	3885	3873	3860	3847	3834	3821	3809	13
88	0 003796	3784	3771	3759	3747	3735	3723	3711	3698	3686	12
89	0 003675	3663	3651	3639	3627	3616	3604	3592	3581	3569	12
90	0 003557	3546	3535	3524	3513	3500	3488	3477	3465	3454	11
91	0 003443	3433	3422	3410	3399	3388	3378	3367	3356	3345	11
92	0 003334	3323	3313	3302	3292	3281	3271	3260	3249	3239	10
93	0 003229	3219	3209	3200	3189	3179	3169	3159	3149	3138	10
94	0 003128	3118	3109	3099	3089	3080	3070	3060	3051	3041	10
95	0 003032	3022	3013	3004	2994	2985	2976	2967	2957	2948	9
96	0 002939	2930	2921	2912	2903	2894	2885	2876	2867	2858	9
97	0 002849	2841	2832	2823	2815	2806	2798	2789	2781	2772	9
98	0 002764	2755	2747	2738	2730	2722	2713	2705	2697	2689	8
99	0 002680	2672	2664	2656	2647	2639	2631	2623	2615	2607	8
100	0 002599	2592	2584	2576	2568	2561	2554	2546	2538	2530	8
101	0 002523	2516	2508	2501	2494	2486	2478	2471	2463	2456	7

volume of the solution determined by boiling the solvent, removing the burner, and reading the volume in the graduated neck before any liquid drains from the walls. Pump and differential thermometer are now inserted, and the liquid pumped over the thermometer bulb until the levels in graduated stem and bulb are constant. Solute is then added, and the pressure difference again read, preferably with a lens, when equilibrium is reached. Calculation of the boiling-point elevation and conversion to centigrade units by reference to Table 17 follow. Values with this thermometer are not subject to changes with atmospheric pressure, to irregularities in the diameter of the capillary bore, or to sticking of the mercury thread, all of which are faults inherent in the Beckmann type. The apparatus should not, of course, be set up in a draft. When water is the manometric fluid, solvents

TABLE 18.—EBULLIOSCOPIC CONSTANTS

Solvent	B.p., °C.	dt/dp	K , Beckmann constant*	K , Menzies working- volume constant
Acetone.....	57.0	26.4	17.2	22.9
Benzene.....	80.1	23.4	26.1	32.0
Carbon disulfide.....	46.3	24.7	23.7	19.4
Carbon tetrachloride.....	76.8	23.3	48.0	32.4
Chloroform.....	61.2	25.2	39.0	27.7
Ethyl acetate.....	77.2	25.1	27.9	33.6
Ethanol.....	78.4	30.3	11.7	15.8
Ethyl ether.....	34.6	26.9	21.6	31.1
Methyl acetate.....	57.1	26.8	20.6	23.4
Methanol.....	64.7	29.6	8.8	11.8

* The change of this constant with barometric pressure is about 0.3 per cent per 10 mm. near 760 mm.

whose boiling points vary from 33 to 101° can be used. Other liquids may be used to reach higher temperatures. From their known vapor pressures and densities the difference of temperature that corresponds to 1 mm. difference in height of the column of filling liquid can be computed, and the results tabulated against the mean temperature of the instrument.

Smith and Milner¹⁶ have reduced the Menzies apparatus to micro proportions. Between condenser and flask the tube is

vacuum-jacketed. A platinum wire is sealed in the bottom to promote smooth ebullition of vapor and liquid. The upper portion of the thermometer is wrapped with a copper-wire spiral in order to insure proper drainage of boiling-hot liquid over the upper bulb. The total height of the apparatus is approximately 25 cm., and boiling points and molecular weights can be determined on as little as 3 ml. of liquid.

58. Boiling Point as a Criterion of Purity.—Constancy of boiling point and purity of liquid are usually considered to go hand in hand. Swietoslawski¹⁷ has devised a more rigorous test, *viz.*, that of identity of liquid and vapor temperatures. The apparatus is a form of his differential ebullioscope in which the distance between liquid and vapor thermometers is lengthened to accommodate a rectifying column 25 to 100 cm. long, depending on the refinement desired. The table below lists his results

TABLE 19.—TEMPERATURE DIFFERENCE BETWEEN LIQUID AND VAPOR FOR VARIOUS SOLVENTS

Solvent	ΔT , °C.
Methanol, free from acetone.....	0.043
Methanol, free from acetone, a second sample.....	0.023
Methanol, synthetic.....	0.000
Ethanol, a commercial grade.....	0.007
Ethanol, dried by means of an azeotropic mixture and distilled in nitrogen.....	0.012
Benzene, purified by an azeotrope.....	0.007
Benzene, a commercial thiophene-free grade.....	0.007
Toluene, purified by an azeotrope.....	0.031
Toluene, a commercial chemically-pure grade.....	0.040
Carbon disulfide, purified and dried in the laboratory..	0.008
Carbon disulfide, the same preparation purified once more.....	0.000

for the ΔT value, *i.e.*, the difference between liquid and vapor temperatures, of a number of liquids. Of this group of solvents, synthetic methanol and a highly purified sample of carbon disulfide were the only ones that were pure. He classifies substances as very pure when the ΔT value is less than 0.040; as sufficiently pure when it is 0.040; relatively pure when it is 0.200; and technically pure when 0.20 to 1.00.

An example of this method's effectiveness in revealing the state of purity is seen in Swietoslawski's results with a

commercial grade of thiophene-free benzene which showed a difference of 0.040° . After distillation a fraction that boiled constantly within a 0.001° limit was found to have a ΔT value of 0.007° . Assuming that the impurity was cyclohexane, some ethyl acetate was added (this compound forms constant-boiling mixtures with naphthenic hydrocarbons but not with benzene), and the distillation once more carried out, whereupon the ΔT value fell to 0.001°C .

59. Determination of Purity or Identity.—Halford¹⁸ has described a method by which boiling-point elevation may be used as an *index of purity*. By comparing with a known substance it can also be used to determine identity of an unknown material. The process is, in general, the same as that for determining molecular weights by elevation of boiling point except that the solvent is usually one in which the substance is not very soluble and a solid phase is present. Excess of solid *A*, containing impurity *B*, is added, and the boiling point observed. The elevation at this point is that due to presence of both *A* and *B* in solution. The solution is next replaced by fresh solvent, the solid phase being allowed to remain in the flask. If all of impurity *B* has been dissolved in the first portion of solvent, the boiling point will now be elevated by an amount due to the presence of *A* only; that is to say, the boiling point of this second portion will be lower than that of the first by an amount related to the number of mols of *B* that were originally present. The absence of all of *B* can be shown by again removing the solvent and adding a third portion, the boiling point of which should be identical with that of the second. This process can be continued until exhaustion of *B* is made certain. Theoretically, from the difference in boiling points between solutions of *A* and *B* mixture and of pure *A*, the number of mols of impurity present in a given weight of *A* can be calculated by means of the equation

$$n = \frac{\Delta T v}{100K}$$

where n = the number of moles of impurity.

ΔT = the difference in boiling points of solutions of *A* and *B*
and of pure *A*.

v = the weight of solvent used.

K = the corresponding constant.

(See Table 19.) If the nature of *A* is known, the mol percentage purity can be calculated; and if that of impurity *B* is also known, the weight percentage purity can be found. Actually, results with this method for quantitative purposes are not reliable, since the boiling-point elevation when two components are present is not always the sum of the single values. This fact is brought out clearly by reference to Halford's data on boiling-point elevation of saturated solutions of several amino acids and their mixtures in methanol or ethanol (see Table 20). It is evident that the value for a mixture of two amino acids, while higher than for either component, is less than the calculated value. Hence,

TABLE 20.—BOILING-POINT ELEVATIONS OF METHANOL AND ETHANOL IN SATURATED SOLUTIONS OF AMINO ACIDS

Amino acids	Elevation of the boiling point in	
	Methanol, °C.	Ethanol, °C.
<i>l</i> -Leucine.....	0.033	0.019
<i>d,l</i> -Leucine.....	0.031	0.013
<i>d,l</i> -Isoleucine.....	0.040	0.025
<i>l</i> -Leucine and <i>d,l</i> -leucine.....	0.043	0.025
<i>d,l</i> -Leucine and <i>d,l</i> -isoleucine.....	0.050	0.037
<i>d,l</i> -Isoleucine and <i>l</i> -leucine.....	0.063	0.037

the method falls short of giving a quantitative estimate of purity but does serve the most useful function of indicating when purity is reached. In the case of 0.05 g. of a mixture containing 10 per cent glycine and 90 per cent *d,l*-alanine, three successive additions of 32 ml. each of ethanol gave elevations of 0.027, 0.021, and 0.021°. The impurity had obviously been removed by the end of the first extraction.

This method of estimating purity is particularly useful when working with compounds that decompose when melted, such as amino, sulfonic, sulfanic, and malonic acids. It has also been applied to triphenylmethyl peroxide and 9-phenylfluorenyl peroxide in benzene solution and to sodium naphthylsulfonates in aqueous solution (see Table 21). The procedure is excellent

as a means of following purification of a compound by digestion rather than by crystallization. Boiling-point tests of a sample of solution after each successive digestion in a solvent often give an indication of attainment of purity. It is possible in this manner to avoid the use of large quantities of solvent necessary for some crystallizations.

60. *Identity of two substances* can be shown by similar methods. Having determined the boiling point of a solution of the known sample in the presence of a slight excess of its solid phase, a quantity of the unknown is added. If the boiling point remains constant, the two substances are identical; if elevated, they are not the same compounds. To avoid erroneous conclusions from insolubility of one of the substances the process should be repeated, reversing the order of addition of the two samples.

61. *Apparatus* needed for this work varies with the sensitivity required. In some cases a mercury thermometer, graduated in

TABLE 21.—ELEVATION OF THE BOILING POINT IN AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

Compound	Elevation of boiling point in °C. when	
	Pure	Mixed
Sulfanilic acid.....	0.25	1.9 4
Disodium 2-naphthyl-6, 8-disulfonate.....	1.7	
Disodium 1-naphthyl-3, 8-disulfonate.....	1.7	

0.1° and contained in a test tube with side-arm condenser, is sufficient. The thermometer is first calibrated in the vapor phase, because a reading when immersed in the liquid is unreliable in the absence of a solid. In the presence of excess solid, readings are consistent to 0.1° with thermometer in the solution. Halford's data in this case are shown in Table 21.

A conventional Beckmann thermometer in a boiling-point apparatus may also be used. In the case of amino acids dissolved in alcohol (see Table 20) this type of thermometer is not sensitive enough and must be replaced by the differential type. When using the method to follow purification of large batches

by digestion, an ordinary flask with a 0.1° thermometer is quite satisfactory. The solid is barely covered with the liquid; the thermometer is inserted; and the mixture refluxed in an oil or other bath for 20 min. or until an equilibrium temperature is reached. After the mother liquor has been filtered in a Buchner funnel, the solid is returned to the flask and again digested. The process is repeated until two successive treatments show the same boiling temperature. Either pure or mixed solvents may be used in this way. In purification of a crude triphenylcarbinol, digestion with petroleum ether has been used regularly in the author's laboratory as a preliminary step to crystallization. By this means alone the melting point can be raised to within 5 or even 2° of the correct value with trifling loss of product.

62. Constant-boiling mixtures occur whenever the composition of the solution equals that of the vapor. The phenomenon is known under the name of azeotropism, and substances that boil together are called azeotropes. Negative azeotropic¹⁹ mixtures have boiling points higher than those of either component; positive ones boil lower. An example of the first class is found in the mixture of formic acid²⁰ (b.p. 100.7°) and water which boil together at 107.1° . The well-known mixture of ethyl alcohol and water illustrates the second class.

63. Among interesting *applications of azeotropism* are *purification* and *separation* of a compound. Mention has already been made (Sec. 21) of the drying of alcohol by a ternary mixture. Purification of large batches of acetone²¹ where the bisulfite method is too cumbersome and the sodium iodide process too expensive has been effected with the 39° constant-boiling mixture of acetone and carbon disulfide. One volume of acetone is mixed with 1.7 volumes of disulfide. Methylal comes over with carbon disulfide at 31° , and the binary mixture with acetone between 38 to 40° . After decomposition with water, acetone is recovered by fractionation. The method is not suitable if separation of methanol is necessary. When a *cis* or *trans* isomer of dibromoethylene is distilled, partial conversion to the other form occurs. Van de Walle²² found that with ethyl alcohol a 108° -boiling isomer came over at 75.6 to 75.9° with 36 per cent alcohol and the 112.50° -boiling isomer distilled at 77.7 to 78° with 67.5 per cent alcohol. Similarly, 700 g. of bromochloro-

ethylene was mixed with 450 g. of alcohol, and a constant-boiling mixture containing 81.9 per cent by weight of a bromochloroethylene, boiling at 75.2 to 75.4°, collected at 66 to 66.6°. The second isomer, whose boiling point was 84.5 to 84.7°, distilled at 72.3 to 72.6° with ethyl alcohol, there being 73 per cent by weight of the ethylenic compound in the mixture. Rissegheem²³ treated the α - β -dibromopropylenes in like manner and found that the 125.95°-boiling isomer distilled at 95.6 to 95.9° with ethyl alcohol (41.95 per cent of dibromide) and the 135.2°-boiling isomer came over at 96.9 to 97.2° with the alcohol (3.45 per cent of dibromide).

64. In *synthesis of esters*, removal of water from the equilibrium mixture is facilitated by constant-boiling mixtures. Taylor²⁴ mixed dry acids such as tartaric, oxalic, succinic, or benzoic acid with alcohol, acidified the solution with alcoholic hydrochloric acid, and refluxed for 20 to 30 min. in a flask provided with an efficient fractionating column and tap funnel. A quantity of benzene, sufficient to remove one-fourth of the water formed in the reaction, was then added, and the mixture distilled until the benzene was removed. This operation was repeated three times, after which the ester, in very high yield, was distilled from the residue. By using a hot-lime tower instead of a rectifying column, Gibson²⁵ found that dry benzene and alcohol would be returned continuously to the flask until reaction was completed. Wuyts and Bailleux²⁶ have studied formation of esters of lactic and tartaric acids refluxing with alcohol, *e.g.*, propyl alcohol, in the presence of *p*-toluenesulfonic acid and removing the 87.7° boiling binary mixture of propyl alcohol (b.p. 97.2°) and water. Similarly, the binary mixture of ethyl alcohol and water distills first when ethyl esters are prepared. Azeotropic methods were used by Contzen-Crowet²⁷ in preparing monoesters (ethyl, propyl, butyl, or amyl) of dicarboxylic acids such as oxalic, succinic, adipic, or malonic. Alcohol, calculated to be sufficient for esterifying just one carboxyl group and for removal of water so formed, was added, the solution refluxed, and the constant-boiling mixture distilled through an efficient fractionating column. In the special case of oxalic acid, occurrence of formates as by-products was prevented by lowering the reaction temperature with carbon tetrachloride, which forms

a ternary mixture with alcohol and water (alcohol 10.3, water 3.4, and carbon tetrachloride 86.3 per cent) boiling at 61.8°. Thus, 90 g. of anhydrous oxalic acid, 100 g. of absolute alcohol, and 460 g. of carbon tetrachloride were refluxed and distilled until the required quantity of water had been collected. The monopropyl ester can also be made by utilizing the ternary mixture of propyl alcohol 11 per cent, water 5 per cent, and

TABLE 22.—BOILING POINTS AND COMPOSITIONS OF CONSTANT-BOILING MIXTURES PRESENT IN SYNTHESIS OF SOME ESTERS
Ethyl Acetate

Components	B.p., °C.	Percentage composition of mixtures boiling at			
		70.3°	70.45°	71.8°	78.15°
Ethyl acetate.....	77.05	83.2	91.5	69.4	
Ethanol.....	78.3	9.0	30.6	95.57
Water.....	100.0	7.8	8.5	4.43
Acetic acid.....	118.5				

Methyl Acetate

Components	B.p., °C.	Percentage composition of mixtures boiling at
		54°
Methyl acetate.....	57	81
Methanol.....	64.7	19

Ethyl Formate

Components	B.p., °C.	Percentage composition of mixtures boiling at
		78.1°
Ethyl formate.....	54.1	
Ethanol.....	78.3	95.57
Water.....	100.0	4.43

TABLE 22.—BOILING POINTS AND COMPOSITIONS OF CONSTANT-BOILING MIXTURES PRESENT IN SYNTHESIS OF SOME ESTER.—(Continued)
Isobutyl Formate

Components	B.p., °C.	Percentage composition of mixtures boiling at	
		79.5°	89.9°
Isobutyl formate	98.3	81.1	
Isobutyl alcohol	108.0	66.8
Water.....	100.0	18.9	33.2
Formic acid.	100.8		

carbon tetrachloride 84 per cent, boiling at 65.4°. Yields of the foregoing monoesters vary from 59 to 82 per cent. Diesters of oxalic acid were prepared in yields of 75 to 85 per cent by Wahl²⁸ who employed either benzene or chloroform as ternary azeotropic agent and sulfuric acid as catalyst. The same author eliminated water with benzene or toluene in the preparation of glyceryl diacetate. Glycerol, 450 g., was heated with 1,260 g. of acetic acid and 1,000 ml. of toluene. The azeotropic mixture boils at 83 to 85° and separates into two layers in the receiver. After 75 to 80 hr., distillation of water ceases, and diacetin, boiling at 155°/15 mm., is recovered. Glyceryl diformate can be prepared similarly.

It is possible for an ester rather than an alcohol to be the principal component of low-boiling mixtures. Such, indeed, is the case with ethyl acetate, data for which, together with those for a number of other esters studied by Wuyts and Bailleux,²⁶ are collected in Table 22.

65. Syntheses of this type are not limited to esters. *Ethers*,²⁹ *formals*, and *acetals*³⁰ likewise have their yields increased when attention is paid to removal of one component by use of a constant-boiling mixture. Tables 23 and 24 give data for a number of reactions studied by Wuyts and coworkers. *p*-Toluenesulfonic acid was frequently used as catalyst for these reactions. Thus, in synthesis of a formal, 120 g. of pulverized trioxymethylene, 50 to 70 per cent excess alcohol, and sulfonic acid (0.5 to 1.0 per cent of the total mass) were mixed and dis-

tilled through an efficient fractionating column. Acetals were similarly prepared using paraldehyde for acetaldehyde.

TABLE 23.—BOILING POINTS AND COMPOSITIONS OF CONSTANT-BOILING MIXTURES PRESENT IN SYNTHESIS OF SOME ETHERS
Ethyl Ether

Components	B.p., °C.	Percentage composition of mixtures boiling at	
		34.15°	78.15°
Ethyl ether.....	34.5	98.7	
Ethanol.....	78.3	95.57
Water.....	100.0	1.3	4.43

n-Propyl Ether

Components	B.p., °C.	Percentage composition of mixtures boiling at		
		74.8°	85.8°	87.7°
<i>n</i> -Propyl ether.....	91	68.1	67.8	
<i>n</i> -Propanol.....	97.19	20.2 <i>h</i> *	32.2	71.7
Water.....	100.0	11.7	28.3

n-Butyl Ether

Components	B.p., °C.	Percentage composition of mixtures boiling at		
		91°	92.6°	117.25°
<i>n</i> -Butyl ether.....	141.9	27.7 <i>h</i>	12
<i>n</i> -Butanol.....	117.5	42.9	62.2 <i>h</i>	88
Water.....	100.0	29.3	37.8	

* *h* signifies that the condensate separates into two layers.

66. Occurrence of constant-boiling binary mixtures is a far more general phenomenon than might at first be supposed if we are to accept the view of Lecat.⁸¹ This investigator has studied innumerable combinations and compiled them in tables. Fenske and coworkers,⁸² on the other hand, have made a thorough

study of petroleum distillation through columns having more than 100 theoretical plates and have concluded that the traditional belief in the impossibility of obtaining pure compounds from such mixtures is not fully justified. Much of the work, therefore, that has hitherto been published on constant-boiling mixtures cannot be accepted as conclusive until confirmed by

TABLE 24.—BOILING POINTS AND COMPOSITIONS OF CONSTANT-BOILING MIXTURES PRESENT IN SYNTHESSES OF SOME FORMALS

Methyl Formal

Components	B.p., °C.	Percentage composition of mixtures boiling at	
		41.8°	42.05°
Methyl formal.....	42.3	92.15	98.6
Methanol.....	64.7	7.85	
Water.....	100.0		

Ethyl Formal

Components	B.p., °C.	Percentage composition of mixtures boiling at			
		73.2°	74.2°	75.2°	78.15°
Ethyl formal.....	87.5	69.5	59.3	90 h*	
Ethanol.....	78.3	18.4	40.7	95.57
Water.....	100.0	12.1	10.0	4.43

Propyl Formal

Components	B.p., °C.	Percentage composition of mixtures boiling at		
		86.4°	87.72°	92.2°
Propyl formal.....	137.14	47.2 h	59.7 h
Propanol.....	97.19	44.8	71.7	
Water.....	100	8	28.3	40.3

* h signifies that the condensate separates into two layers.

TABLE 24.—BOILING POINTS AND COMPOSITIONS OF CONSTANT-BOILING MIXTURES PRESENT IN SYNTHESIS OF SOME FORMALS.—(Continued)
Butyl Formal

Components	B.p., °C.	Percentage composition of mixtures boiling at	
		92.6°	98.2°
Butyl formal.....	181.8	38 h
n-Butanol.....	117.5	62.2 h	
Water.....	100.0	37.8	62

n-Amyl Formal

Components	B.p., °C.	Percentage composition of mixtures boiling at	
		95.4°	99.2°
<i>n</i> -Amyl formal.....	222.9	7.0 h
<i>n</i> -Pentanol.....	138.0	55.3 h	
Water.....	100.0	44.7	93.0

study with a highly efficient column. But it is unquestionably true that ordinary laboratory fractionation will not be effective in separating a vast number of mixtures. No absolute rule for predicting azeotropism can be set forth. In general, substances³³ that are chemically dissimilar and have boiling points reasonably near each other are apt to form constant-boiling mixtures. Strong molecular association is sufficient if it occurs in only one constituent. Mixtures with minimum boiling points are characterized by cooling, and those with maximum boiling points by warming on mixing. No ternary mixture³⁴ with a maximum boiling point is known, and no alcohol with a boiling point higher than 108° should form a ternary azeotropic mixture with hexane and water or form a binary mixture with benzene. Data³¹ for a few binary azeotropic mixtures are collected in Table 25.

67. *Separation of constant-boiling mixtures* may be effected³⁵ by distilling at another pressure. Composition is dependent

TABLE 25.—SOME BINARY AZEOTROPIC MIXTURES

Components				Azeotropic mixture	
A	B.p., °C.	B	B.p., °C.	Mol % A	B.p., °C.
Water.....	100	Hydrochloric acid	-85.0	88.9	110.0
Water.....	100	Hydrobromic acid	-67.0	83.1	126
Water.....	100	Hydriodic acid	-35	84.3	127
Water.....	100	Nitric acid.....	86	43.3	107.1
Water.....	100	Ethanol	78.5	10.6	78.2
Water.....	100	<i>n</i> -Propanol	97.8	56.8	87.7
Water.....	100	iso-Pentanol	130.5	82.8	95.2
Water.....	100	Benzene	79.6	29.6	69.3
Water.....	100	Toluene	110.5	44.4	84.1
Chloroform.....	61.2	Methanol	64.5	65	53.5
Chloroform.....	61.5	Ethanol	78.5	84	59.3
Carbon tetrachloride.....	76.8	Methanol	64.5	44.5	55.7
Carbon tetrachloride.....	76.8	Ethanol	78.5	61.3	65.0
Carbon tetrachloride.....	76.8	Ethyl acetate	77.1	43	74.8
Carbon tetrachloride.....	76.8	Methylethylketone	79.6	53.4	73.8
Carbon disulfide.....	46.3	Methanol	64.5	72	37.7
Carbon disulfide.....	46.3	Ethanol	78.5	86	42.4
Carbon disulfide.....	46.3	Acetone	56.1	61	39.3
Carbon disulfide.....	46.3	Ether	34.5	1	34.5
Formic acid.....	100.5	Benzene	79.6	21	71
Formic acid.....	100.5	Toluene	110.5	66.7	85.8
Nitromethane.....	101.9	iso-Butanol	107.3	70	94.7
Acetic acid.....	118.1	Benzene	79.6	2.5	80.1
Acetic acid.....	118.1	Toluene	110.5	27.3	105.4
Acetic acid.....	118.1	<i>m</i> -Xylene	139.0	60	115.4
Acetic acid.....	118.1	Chlorobenzene	132.1	72.5	114.7
Ethanol.....	78.5	Benzene	79.6	44.8	68.2
Ethanol.....	78.5	Toluene	110.5	81	76.7
Ethanol.....	78.5	<i>n</i> -Heptane	98.4	67	72
Ethanol.....	78.5	Ethyl acetate	77.1	46	71.8
Ethanol.....	78.5	Ethyl bromide	38	7	37.6
Ethanol.....	78.5	Cyclohexane	81.4	44.5	66.7
<i>n</i> -Butanol.....	117.7	Toluene	110.5	37	105.5
<i>n</i> -Butanol.....	117.7	<i>n</i> -Butyl acetate	126.5	56	113.5

on relative vapor pressures which will not remain constant as total pressure is altered. In fact anhydrous alcohol can be prepared from the constant-boiling product by distilling at 27.96° under 70 mm. pressure. Another method is to add a third

component in order to obtain a ternary mixture. Addition or removal of water, freezing, and chemical reactions involving one component are also convenient methods at the chemist's disposal.

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CHAPTER IV

FRACTIONAL DISTILLATION

68. One of the most important laboratory operations is the separation of compounds by distillation. Yet until recent years efficient apparatus has been lacking. Thanks to the interest of petroleum chemists, and particularly to that of Fenske and coworkers, a high state of perfection in designing columns has been reached. It is now possible to build columns that will separate compounds boiling only 2° from each other. These developments make obsolete all other types of fractionating apparatus. Exact knowledge of the efficiency of any column is a prerequisite to its use, if disappointments in its performance are to be avoided. Neither has the micro field been left untouched. The information that can be acquired from minute amounts of liquid is indeed astonishing. The purpose of this chapter is to emphasize these modern aspects of an old art.

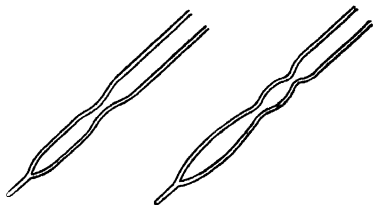


FIG. 28.—Emich fractionating tubes.

69. Micro and Semi-micro Scale.—The *Emich*¹ tube, which is the simplest apparatus for this purpose, consists of a capillary tube about 65 mm. long and 3 mm. inside diameter (see Fig. 28). For convenience in handling, a glass rod is sometimes sealed to the bottom. Clean dry asbestos, to absorb the liquid and insure smooth distillation, is added, and a few drops of liquid forced by centrifuging into intimate contact with it. Wet filter paper, wrapped around the tube above the constriction, serves as a condenser. The liquid is next distilled by carefully heating the tube, kept vertically or at an angle of about 45° in a bath or metal block. If a minute free flame is used, the tube

should be held and rotated at least 5 cm. above it. A ring of condensate slowly ascends the tube until it passes the constriction. Heating is then stopped, the drop of distillate removed by a capillary, and its boiling point determined by the Emich method previously described (Sec. 54). The distillation tube is next centrifuged, and the operation repeated until no more distillate is obtained. By this means 20 cmm. (0.02 ml.) of a mixture of alcohol and acetone (80 per cent alcohol) was separated into eight fractions whose boiling points were as follows:

	°C.
First.	61 -66.5
Second	61 -68.5
Third.	66.5-73.0
Fourth.	66.5-73.3
Fifth.	68.5-75.5
Sixth.	68.5-76
Seventh.	73 -77
Eighth.	73 -77.5

To obtain pure alcohol and pure acetone the lower boiling portions would have to be fractionated repeatedly. This method is of greatest importance when working with minute quantities of material.

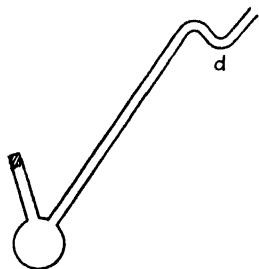


FIG. 29.—Micro fractionation apparatus of Gettler, Niederl, and Benedetti-Pichler.

70. An apparatus used for fractionating alcohol from 5 ml. of water solution is described by Gettler, Niederl, and Benedetti-Pichler¹ (see Fig. 29). A water solution is placed in a bulb of about 12-ml. capacity, zinc dust being added to prevent bumping and secure even distillation. After the upper part of the flask has been dried by careful heating, a piece of wet filter paper is wrapped around the receiver

d, and a ring of distillate driven up the tube and collected in the receiver. The flame is then removed, and the drop collected by inserting a capillary pipette. A boiling point can be determined on this drop as collected or after refractionation in an Emich tube. The relatively long straight tube above the distilling flask enables an operator to obtain a considerable degree of fractionation. The apparatus is extremely useful for obtaining minute quantities

of liquid from a larger body of solution. A similar apparatus² has been employed in quantitative isolation of ether from dilute solutions. For this purpose the upper portion of the tube is bent downward so that the distillate collects in a calibrated centrifuge tube. The distillation flask also has an opening for filling or siphoning. It is important in this as in all micro distillations that the apparatus be cleaned with cleaning solution, rinsed, and dried by heating in a current of dry air. As small an amount as 37 out of a possible 44 mg. of ether has been recovered from 50 ml. of solution by this method.

71. The experience of Rose³ with vertical, 3- and 6-mm. vacuum-jacketed fractionating columns 1 ft. long can well be adapted to micro work. The evacuated tube was silvered and attached in a vertical position to a flask. At a reflux ratio of 70:1 he obtained as high as 17 theoretical plates (see Sec. 82), and his results were better when the column was empty instead of packed. At low rates of boiling, operation of such columns becomes increasingly difficult because the slightest variation in heat input or insulation destroys the equilibrium conditions. He believes that at very low rates, with the column insulated almost as well as in a calorimeter, an efficiency as high as 30 plates might be attained. Such perfection would indeed be remarkable in fractionating liquids.

72. An excellent apparatus modeled closely after the conventional type of distillation flasks and constructed from small tubing has been described by Peakes.^{4a} Although originally designed for distillating 0.5 to 1 ml. of liquid under vacuum, it may be used also at atmospheric pressures. To insure uniform draining, it should be well cleaned with cleaning solution, washed with methanol, and dried before use. If the distance from bulb to side arm is made longer, a certain amount of fractionation is possible. Heat is supplied from a small oil or metal bath, and bumping is prevented by a pledget of glass wool. Craig^{4b} has constructed a novel micro apparatus by sealing a condenser above an enlarged Siwoloboff tube.

MACRO FRACTIONATION

73. Factors in Design of a Column.—As far as apparatus is concerned, sharpness of any separation depends upon insu-

lation, packing, reflux ratio, and height of the column. On theoretical grounds a fractionation if it is to be efficient should occur under reasonably good adiabatic conditions. It is obvious that the necessary equilibrium conditions between downflowing liquid and upward-moving vapors cannot be established if too much cooling is taking place on the walls of the column. One of the practical methods of achieving *good insulation* is by use of a silvered evacuated jacket. Efficiency of these jackets depends upon the care with which they are cleaned, silvered, and exhausted. Excellent directions have been published⁵ for this operation. Insulation of this type is particularly valuable when the compound boils below room temperature. Its serviceability diminishes considerably at higher temperatures. Above 100° it is necessary to resort to other methods if the column is to give a satisfactory performance.

Commercial pipe covering, if sufficiently thick, has been claimed⁶ as a very suitable insulating material. In Table 26 the heat loss through commercial pipe covering is compared with that from a black-body vacuum and a silvered evacuated surface. In an actual test at 100°C., using a condensation method, a 2-ft. standard 2.5-in. pipe, insulated by commercial rock wool

TABLE 26.—HEAT LOSS FROM STANDARD 2.5-IN. (63.5-MM.) PIPE AT ROOM TEMPERATURE (21.1°)

Temp. of pipe, °C.	Heat loss in B.t.u. per lineal foot per hour			
	Black- body vacuum	Silvered vacuum	Commercial steam pipe covering	
			1.5 in. thick	3 in. thick
93.3	135	21.7	41	28
197.2	533	85	107	73
298.9	1280	205	180	122

covering 4 in. thick, showed 27.5 B.t.u. loss per lineal foot per hour. A 3-ft. pipe of similar size but insulated by 85 per cent magnesia covering of the same thickness gave 29.7 B.t.u. per lineal foot per hour when the room temperature was 20°C. These values were uncorrected for end losses. With smaller

size pipe the relative advantage of commercial pipe covering decreased; with larger sizes it increased. Since efficiency of a silvered evacuated insulation depends upon the care with which the operation is performed, comparisons given in the preceding table do not necessarily state the relative behavior of all such jackets.

74. A decided improvement over mere care to use the best insulation is the *application of heat to balance the loss*. Fenske, Quiggle, and Tongberg⁷ insured an adiabatic condition by first encasing the column with 85 per cent magnesia pipe covering 2 in. thick, then wrapping the outside with $\frac{3}{8}$ -in.-wide chromel resistance ribbon 35 Brown and Sharpe gauge, and finally adding another 1-in. layer of magnesia pipe covering on the outside. The heating unit was divided into three sections so that the temperature at the top, middle, and bottom could be controlled separately and made to agree with that at corresponding levels on the inside of the column. In an apparatus of Peters and Baker⁸ the heating wire was wrapped on asbestos tape surrounding the column. Nichrome wire (0.016 in.) with three to four turns per inch was used where the temperature was to be maintained between 100 and 200°C. Commercial insulation surrounded the wire. Bush and Schwartz⁹ wrapped their heating unit on the outside of the glass jacket and surrounded the whole with an evacuated jacket. Resistance wire should never be placed directly on the wall of the fractionating column.

A glass double-walled container¹⁰ through which cold alcohol was pumped from a constant-temperature reservoir was employed in the fractionating apparatus of Kistiakowsky and coworkers for separation of butene isomers. The column itself was passed through the opening in the center of the jacket so that it was air-jacketed from the outside cooling jacket. This arrangement provided a continuous heat gradient from bottom to top which could be adjusted by varying the rapidity with which the liquid was pumped. For use at higher temperatures the alcohol was replaced by oil.

In the author's laboratory, hot Nujol is driven through a 2-ft. double-walled Thiele-tube insulating jacket by means of a stirrer which turns in a side tube (see Fig. 30). Propeller blades, extending almost to the glass wall of the tube, are securely

mounted on a shaft passed through two ball bearings. Heat is applied with a gas flame or resistance wire on the bottom portion sloping up to the jacket. A 3- to 5-mm. air space separates the fractionating column from the jacket. Temperatures as high as 250° have been reached, although at this point it would be better to avoid hazards from sudden breakage by operating at reduced pressure.

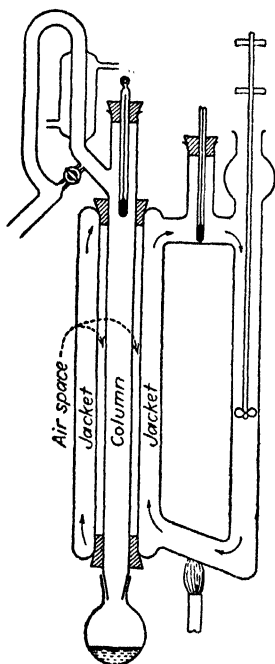


FIG. 30.—Thiele-tube insulating jacket.

75. Nature of the Packing.—The *Podbielniak column*¹¹ has a continuous wire, Brown and Sharpe gauge No. 20, spiral for a packing. It is made with six or seven turns per inch, and is fitted into a tube 3.8 mm. in diameter. The special feature claimed for this type of packing is that the refluxed liquid distributes itself into very thin capillary films, supported only at their boundaries by the turns of the wire coil and by the glass wall, rather than merely wetting the very small surface of the packing. A maximum contact between liquid and vapor with minimum holdup of liquid results. Such specifications for tube diameter and packing have been found from numerous studies to be the most effective possible for this type of construction. To secure a snug fit the wire

coil is ground or filed on the outside. The spiral also facilitates draining, since it has been shown that slugs of liquid are less apt to be entrained in a column which has a spiral packing than in an unpacked one of the same size. Podbielniak columns were originally designed for fractionating gasoline. In an organic laboratory metal wires are corroded easily. Glass spirals of the proper dimension can be made by simultaneously drawing out and winding softened pyrex rod on a steel drill rod $\frac{3}{32}$ in. in diameter after the manner described later for the preparation of the Fenske spirals (see Sec. 77). This packing is not at all difficult to make and proves extremely satisfactory where minimum holdup is essential.

76. Ring Packing.—Cylindrical tubes or rings, usually with length equal to diameter, have been found to be reasonably satisfactory in fractionating columns. Effectiveness (H.E.T.P., see Sec. 82) is inversely proportional to ring diameter as judged by relative efficiency values determined by Peters¹² on a mixture of acetic acid and water (see Table 27). Increased efficiency with diminishing ring size was also found by Leslie and Geniesse,¹³ who used 6.5- and 5.6-mm. Lessing rings with a chloroform-

TABLE 27.—VARIATION OF EFFICIENCY WITH RING DIAMETER

Diameter, Inches	H.E.T.P., Inches
1	52
0.625	23
0.25	10
0.125	6

toluene mixture. There is a practical lower limit in diameter, for Peter, Jr., and Baker⁸ reported that glass rings smaller than 5 by 5 mm. outside diameter showed undue obstruction both to upward flow of vapor and to downward run of reflux. The holdup in a column 12.8 mm. in diameter by 1.22 in. (4 ft.) long with 5-mm. diameter filling was about 15 ml. In place of tubing cut to the desired length it is possible to purchase from an ornament dealer hollow cylindrical glass beads 3.2 mm. inside diameter by 6.4 to 4.8 mm. long. Evans⁶ and coworkers claimed satisfactory results with these, although no comparison data are given.

77. Single-turn Helices.—A most careful and complete study of the use of helices, glass rings, and other packing material is reported by Fenske¹⁴ and coworkers. Their comparisons between jack chains, glass tubes, and wire helices of one, two, and six turns are presented in Table 28. From such data it is possible to draw the following conclusions: Efficiency, as measured by the H.E.T.P. value, of wire helix packing increases about threefold for an increase from 11.38 to 20.30 cm. of surface per centimeter of packing. Efficiency of wire helix packing increases with liquid holdup which, in turn, increases with surface area of packing per unit of volume. The single-turn wire helix is more effective than one with a greater number of turns. Indeed, with the exception of a brief mention by Rose³

of results with glass triangles, the literature contains no description of packing that is superior to single-turn spirals.

TABLE 28.—EFFICIENCIES OF DIFFERENT TYPES OF PACKING AS DETERMINED WITH CARBON TETRACHLORIDE-BENZENE MIXTURE

Packing	Free space, %	Surface area,* sq. cm./cc.	Reflux ratio	Vapor velocity at top, ft./sec.	H.E.T.P., in.	Holdup, ml. liquid/ml. packing
Jack chains	76	6.73	0.942	0.875	3.58	0.029
			0.939	0.857	4.09	
			0.901	1.780	3.48	
Glass tubes 0.22 by 0.22 in.	66.2	4.46	0.947	0.749	3.38	0.089
			0.890	0.863	3.82	
			0.949	0.877	3.29	
			0.938	0.864	3.67	
1-turn helix	79.8	22.30	0.951	0.835	1.82	0.129
			0.973	1.452	2.13	
2-turn helix	85.5	14.40	0.940	0.879	4.82	0.110
			0.939	1.410	3.57	
			0.969	1.482	2.74	
6-turn helix	88.4	11.38	0.955	0.855	5.33	0.082
			0.970	1.719	7.02	
			0.988	1.760	6.20	

* Surface area does not include column wall.

Methods of preparing such filling from glass rod has been described in great detail by Wilson and coworkers,¹⁵ by Roper and coworkers,¹⁶ by Young and Jasaitis,¹⁷ and by Stewart.¹⁸ A brass or steel rod 3.2 mm. (approximately $\frac{1}{8}$ in.) in diameter and 31 to 75 cm. long is adapted to catch one end of a 2- to 3-mm. glass rod by either flattening and drilling a hole in the end of the metal rod or slotting the end and bending the prongs to fit the glass rod. To facilitate removal, the metal rod may be made slightly conical on the drilled end by rubbing with emery paper, and the winding form is given a very thin coat of natural graphite by rubbing with a cloth upon which graphite has been sprinkled

together with a drop of lubricating oil. The end of the glass rod is inserted in the afore-mentioned metal catch and heated to softening in a moderate Bunsen flame if it is soft glass or in an oxygen flame about 4 cm. high if it is pyrex. A simple bearing may be used for the left end of the winding form. The metal rod is rotated by hand or motor while the glass rod is fed on to the winding form at the desired angle. With a little practice, uniform spirals can be wound. Long spirals are easily removed when cooled, but it is convenient to nick them with a glass marking pencil while still on the rod. Upon squeezing the spiral between thumb and forefinger, each turn is broken at the nick. Smaller pieces fall off the rod.

Using 75 per cent single and 25 per cent double turns of this packing, Wilson and coworkers found that the H.E.T.P., as

TABLE 29.—EFFICIENCIES OF VARIOUS LABORATORY COLUMNS PACKED WITH SINGLE-TURN GLASS HELICES

Diameter, in.	Height of packing, in.	Theoretical plates, total	H.E.T.P., in.
0.43	10.3	10.0	1.1
0.51	15.0	6.0	3.0
0.32	15.8	7.7	2.4
0.55	17.3	9.6	2.0
0.51	17.3	12.5	1.5
0.55	17.7	12.0	1.6
0.36	20.9	15.0	1.5
0.63	23.6	10.7	2.4
0.51	24.8	10.0	2.7
0.67	32.2	13.5	2.6
0.59	34.7	19.5	1.9
0.55	53.1	22.3	2.5

determined by distilling a mixture of benzene and carbon tetrachloride, was 1.8 in. (4.57 cm.) in a total condensation, variable take-off column with a packed section of 44 by 1.4 cm. and was 2.0 in. in a similar column with a 40- by 0.8-cm. packed section. The H.E.T.P. with 5- by 5-mm. glass tubes in a similar 40- by 1.4-cm. column was 4.0 in. (10.2 cm.). With coils of approximately one turn, fiber diameter 0.6 mm., and coil diameter equal to 4.4 mm. made from a long helix with adjacent coils

practically touching, the weight of 300 individual coils was 2.43 g., and the volume was 5 ml. measured in a graduated cylinder of 17 mm. inside diameter. In a column 4.6 m. by 16 mm. inside diameter containing 50,000 to 60,000 coils the total volume of the glass was equal to 194 ml., the surface was 14,000 sq. cm., and the free space about 80 per cent. Fenske¹⁴ reports that efficiencies of a number of laboratory columns packed with glass helices of three-fourth to two turns (see Table 29)

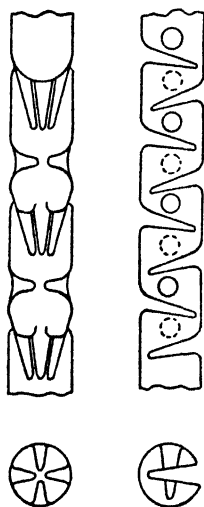


FIG. 31.—Types of Vigreux column.

were higher than that obtained for a column 0.78 in. in diameter and 27 in. long, filled with 0.25- by 0.25-in. rings, for which an H.E.T.P. of 6 in. was obtained. He also found that a column of the Vigreux type, 0.43 in. in diameter and 27 in. high with indentations regularly spaced and shaped to give maximum vapor-liquid contact, had an H.E.T.P. of 5.4 in.

78. Vigreux¹⁹ columns can be classified as packed columns, since the indentations serve to fill inside space and provide more surface on which equilibrium conditions are established. The column is a simple one to make. A spot on the wall is heated and pressed in with the sharp point of a file, wire, or other small tool. Figure 31 shows one type of construction.

(For comparison with some other columns see Sec. 77 and 81.) The small holdup in this column, as in the Podbielniak, makes it suitable for fractionating small quantities of liquids.

79. The Reflux Ratio.—For efficient fractionation a high percentage of vapors which traverse the length of the column must be condensed and returned. The still head which accomplishes this object may be either the *partial-condensation* or the *total-condensation* variable take-off type. In the former a portion of vapor is condensed by the dephlegmator and returned to the column to furnish reflux, while the remainder is let through to the receiver. Careful adjustment of heat interchange in the dephlegmator can be had by adjusting the water inlet with stop-cocks, by using constant-level devices, by controlling thermostatically the temperature of the water, or by varying the

distance to which the condenser projects into the vapor stream. The very ingenious regulator of Othmer²⁰ for adjusting temperature automatically in large units is worthy of special reference.

The second type of still head, *total-condensation variable take-off*, requires that all vapor be condensed, a portion of condensate returned to the column, and the rest collected in the receiver. Several advantages are apparent in this arrangement. True equilibrium conditions are established before any distillate is collected—a particularly important point when the jacket temperature has to be set. Moreover, reflux is more easily controlled, since careful adjustments in the dephlegmator are unnecessary. Especially is this kind of still head satisfactory when changing from a lower to a higher boiling fraction. The stop-cock is closed, and the liquid allowed to reflux until the thermometer records the lowest temperature possible. The column has then reached an equilibrium condition and is effecting its maximum degree of separation. The cock is then opened, and a little distillate drained into the receiver. Again the cock is closed, and equilibrium conditions once more established. By continued opening and closing of the cock, separations become sharper. Holdup of reflux at the take-off should not be too great if sharp cuts are to be obtained. For this reason a capillary tube is usually employed to drain condensate to the receiver. The still head of Whitmore and Lux²¹ (Fig. 32), suitable for use at any pressure, is very satisfactory. A conventional shallow circular trough design is illustrated in Fig. 33.

If a small cup is inserted in the still head, as in the type used by Brunu²² (Fig. 34), the column can be used in a batch-stripping process. A portion of condensate is returned to the column for reflux until equilibrium conditions have been attained, after which the contents are drained to the receiver. In this manner small quantities of low-boiling constituents can be separated without distilling the whole batch.

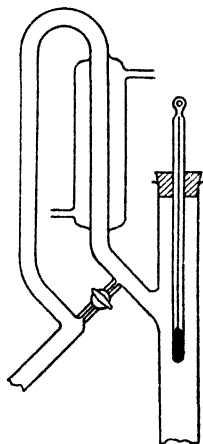


FIG. 32.—Total-condensation variable take-off still head of Whitmore and Lux.

The importance of a high reflux ratio is obvious, since it permits better separation of constituents in a single passage. Ratios as high as 30:1 are common, and values of 50 or 70:1 have been obtained. Amount of reflux must never be raised to a point where flooding occurs, for slugs of liquid reduce the effective area of the packing. Reflux ratio is defined as the amount of liquid returned to the column over the amount collected as distillate. It is also expressed sometimes as the ratio of heat required to

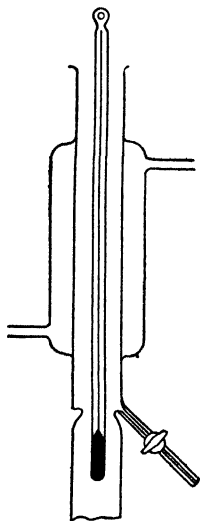


FIG. 33.—Total-condensation variable take-off type of still head.

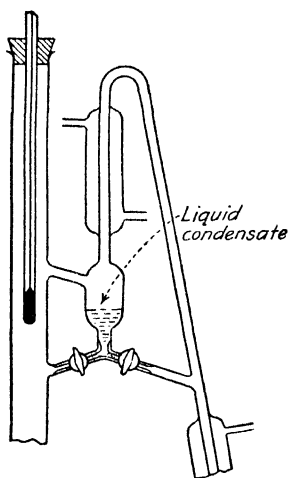


FIG. 34.—Still head of Bruun, arranged for control of take-off or for batch stripping of small amount of low-boiling concentrate.

volatilize liquid runback divided by total latent heat in the vapor passing up through a horizontal cross section.

80. Length of Column.—A final factor in the performance of any column is its length, since this obviously will increase the number of theoretical plates and thereby the completeness of fractionation. With packed columns height becomes chiefly a matter of the amount being distilled, the quantity of permissible holdup, and the overhead space. Although very tall columns have a great number of theoretical plates, it is also true that efficiency per unit length is reduced, a fact explained by Fenske¹⁴

as being due to a greater tendency to channel. The effect is most noticeable where column diameter is small (0.75 in.) and is not always discernible when the diameter is 2 in. In the latter case channeling is apt to occur even in short sections. For ordinary laboratory purposes a packed section 10 to 24 in. high and $\frac{1}{3}$ to $\frac{1}{2}$ in. in diameter will give 7 to 15 theoretical plates. With 12 plates, complete separation of benzene and toluene is theoretically possible.

There are a number of unpacked columns which depend upon great length by a spiral path to obtain fractionation. The *Widmer*²³ column has a spiraled solid glass rod which fits snugly between a central glass rod and an outer glass tubing. A double jacket surrounds the spiral core so that hot vapors from the distilling flask pass upward through the outermost section and downward through the next section before passage up the spiral. In this manner the inner spiral column is kept warm by the hot vapors that surround it. Condensate in the column is returned to the distilling flask through a trap. The whole apparatus can be surrounded with an air or other jacket for further insulation. The column has a theoretical disadvantage since the spiral is jacketed with vapors necessarily hotter than itself. In comparison with packed columns this type suffers from its more complicated construction, its lack of great efficiency, and its useless subjecting of compounds to decomposition in the long vapor path.

*Dufton*²⁴ made his spiral from wire wrapped about an inner rod as a core, over which a closely fitted outer tube furnished the remaining essential part for a spiral partition. The corrosion problem inherent in use of metal was avoided by *Davis*,²⁵ who used a spiral glass tube surrounded with a vacuum jacket. Glass tubing 5 mm. in diameter and 3 to 5 m. long was wound into a spiral of 30 to 40 turns with a low pitch. The whole was surrounded by a silvered and highly evacuated jacket, with a cup recessed in the top surrounding the upright head of the spiral. In this cup a cooling liquid was placed to serve as a dephlegmator. The spiral construction has enough flexibility to reduce strains existing in the glass during distillation. A major point affecting efficiency is the care in silvering and evacuating the jacket, but even with the greatest precaution in this operation the insulation

functions poorly at temperatures of 100° and higher. The column was designed for fractionating low-boiling petroleum fractions, a purpose for which it is very effective.

81. Measurement of Efficiency of a Column.—Efficiency of a number of columns has been expressed by Hill and Ferris²⁶ in terms of a *constant calculated from the enrichment ratio*. The mathematical expression of the latter is

$$E = \frac{C_D(1 - C_L)}{C_L(1 - C_D)}$$

where E = the enrichment ratio.

C_D = the molar concentration of carbon tetrachloride in the distillate or vapor.

C_L = the molar concentration of carbon tetrachloride in the still.

For mixtures of carbon tetrachloride and benzene, the value of E from a series of determinations of the vapor-liquid equilibrium curve was found to average 1.18. The constant for the column was then calculated by the equation

$$\frac{C_D}{C_L} = 1.18^K \quad \text{or} \quad K = \frac{\log C_D - \log C_L}{\log 1.18}$$

where K = the constant for the column or still under consideration. In Table 30 values of K for varying reflux ratios are given

TABLE 30.—EFFICIENCY OF DIFFERENT TYPES OF COLUMNS ACCORDING TO HILL AND FERRIS

Reflux ratio K	Plain tube	Pear	Wurtz	Lebel- Henn- inger	Glinsky	Vig- reux	Packed with 5.5- by 5.5- mm. glass tubes
1*	0.9	1.0	1.1	1.1	1.3	1.2	1.3
2	...	0.9	0.8	0.9	1.3	1.4	1.4
5	...	0.8	0.5	1.1	...	1.5	1.4
9	...	0.8	...	0.9	...	1.4	1.9

* No insulation in this series with reflux ratio equal to 1.

for a number of columns of equal length, with rate of distillation maintained at 1 ml. per minute. It is apparent that the Wurtz,

Pear, and Lebel-Henninger columns are little better than unpacked tubes and have less efficiency with controlled reflux. At the highest reflux ratio the packed column is the most satisfactory.

82. A simple and common method of comparison is by measurement of the *height equivalent to a theoretical plate*, the H.E.T.P. value. For a plate to be theoretically perfect it is necessary that vapors be in phase equilibrium with the liquid through which they pass. In the case of packed towers²⁷ the length of packing required to do the work of one theoretical plate is termed the H.E.T.P. A sample of condensed vapor taken from the top of this distance would be in phase equilibrium with a sample of liquid from the bottom. Lewis²⁸ has pointed out that with liquids having boiling points not too far distant from each

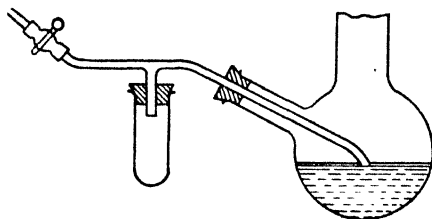


FIG. 35.—Flask used in determination of the theoretical plate value.

other and belonging to the same class, *i.e.*, both liquids associating or nonassociating, a mol of high-boiling constituent will be condensed for every mol of low-boiling constituent volatilized. This fact follows from the approximate constancy of Trouton's rule. The determination for short columns is usually made with mixtures of benzene and carbon tetrachloride, the data of Rosanoff and Easley²⁹ being used for the composition of gaseous and liquid phases. Graphs should be made on a large piece of cross-sectional paper if results are to be of any value. With mixtures of benzene and toluene the data of Rosanoff, Bacon, and Schulze³⁰ are available. For long columns those of Tongberg, Quiggle, and Fenske³¹ on *n*-heptane and methylcyclohexane are necessary.

The distillation apparatus must be arranged so that samples can be taken simultaneously from the flask and top of the column.

For this purpose the flask is provided with a small tube (e.g., see Fig. 35) through which a sample can be withdrawn by suction into a test tube. The column is operated under total reflux, *i.e.*, with no collection of condensate in receiver. Ample time should be given to attain equilibrium conditions before

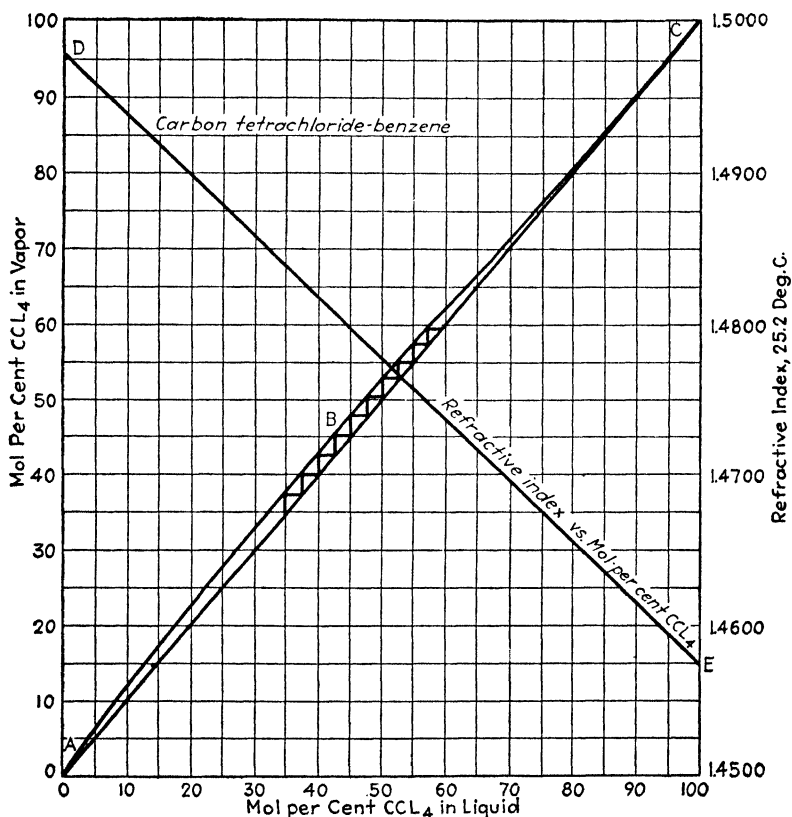


FIG. 36.—Graphical method of finding the number of theoretical plates.

drawing off samples for analysis. The composition of the two fractions is determined by measuring their refractive indices. A series of steps between vapor- and liquid-composition curves (see Fig. 36) can now be drawn. The number of these steps, less one for the still itself, is the total number of theoretical

plates. The height of packing divided by the number of plates is the height equivalent to a theoretical plate. More than one determination should be made.

Several interesting facts have been expressed in H.E.T.P. values. Reference has already been made (Sec. 76) to the fact that the H.E.T.P. becomes smaller with decreasing diameter of rings. For mixtures of compounds of equal molecular weight, lower values will be found where attraction of unlike is less than that of like compounds for each other. The value of the H.E.T.P. is greater for compounds of high molecular weight. In other words, separation of substances of high molecular weight requires a column longer than is necessary for lighter compounds. The variation may be seen in Table 31 where data²⁷ for various mixtures, fractionated through a column packed with 0.25-mm. rings, are given. Carswell's³² explanation is that the vapor

TABLE 31.—VARIATION OF THEORETICAL PLATE VALUE WITH DIFFERENT MIXTURES

Compound	H.E.T.P., Inches
Ethyl alcohol and water, below 88%.....	3.65
Ethyl alcohol and water, above 88%.....	4.2
Methyl alcohol and water.....	3.0
Acetone and alcohol.....	6.0
Nitric acid and water.....	8.0
Acetic acid and water.....	10.0
Benzene and toluene.....	10.0

volume at the boiling point of unit weight of substance is indirectly proportional to molecular weight and directly proportional to absolute temperature. Therefore in the case of a high-molecular-weight substance an equal volume of vapor comes in contact with a reduced quantity of backflow. The surface of the backflow liquid also varies indirectly with the density. Hence it follows that the H.E.T.P. value is related to molecular weight, density at the temperature involved, and absolute boiling point by the equation

$$\text{H.E.T.P.} = k \frac{Md}{T}$$

where M , d , and T represent in order the above-mentioned factors

and k is a constant. Table 32 shows the results of applying this equation to a number of mixtures.

TABLE 32.—RELATION OF H.E.T.P. VALUE TO MOLECULAR WEIGHT

Mixture	H.E.T.P., cm.	Mol. weight ave.	B.p., °A.	d	k^*
Ethyl alcohol-water, below 88%...	9.2	31.4	366	0.86	92
Ethyl alcohol-water, above 88%...	10.7	39.9	351	0.83	78
Methyl alcohol-water.....	7.6	24.5	355	0.87	96
Acetone-ethyl alcohol.....	15.2	51.3	341	0.86	86
Benzene-toluene.....	25.4	84.4	368	0.80	88

* The average value of k is 88.

If Carswell's³² equation is valid within certain limits, efficiency may be related to column free space and surface of liquid backflow by the formula

$$\text{H.E.T.P.} = C \frac{V}{S}$$

where V = the volume of vapor space.

S = the surface of packing.

C = the constant of proportionality.

This equation informs us that under ideal conditions, column diameter has no effect on efficiency, for the number of rings per unit volume will be the same irrespective of diameter, and the ratio V/S will therefore be constant. Indeed, if wall area is reckoned in the equation, efficiency under ideal conditions should improve as the diameter decreases. Practically, this result may not be reached because of variations in the arrangement of packing adjacent to the wall. The equation may be further simplified for the purpose of comparing the effect of varying radius of rings contained in a unit volume of packing, whereupon H.E.T.P. becomes equal to Cr , where C is a constant and r is the radius. Tests, with acetic acid-water mixtures, of this equation, suitable allowance being made for effect of changing radius on surface and free space, show (Table 33) an average value of C equal to 47, but the deviation from average suggests that other factors are also involved. Fenske and coworkers have pointed out

the lack of uniformity with which packing fills a column and makes contact with the walls, as well as the variations in channeling. Such unevaluated factors combine to cause variations in columns packed with the same material. These investigators have also shown that the possible behavior of a column may be approximated from the surface area and the percentage of free space. The product of the number of square inches of surface area per cubic inch of packing and the percentage of free space divided by 100 gives a numerical rating that parallels the utility of the packing. This statement merely affirms that two items of major importance for high efficiency are maximum surface combined with maximum free space.

TABLE 33.—EFFECT OF VARYING RADIUS OF PACKING RINGS ON THEORETICAL PLATE

Mean radius of packing	H.E.T.P., cm.	C
0.16	10	62
0.32	14	44
0.64	25	40
1.58	63	39
2.54	132	52

83. Fractionating Columns.—From the types of insulating material and packing already described, it should be possible for anyone to construct a fractionating column for general laboratory use that is far superior to older forms. The few columns mentioned in this and the following section are included in this account not because they happen to be ideal but because they are representatives of methods of assembly that may be distinctly helpful.

*Doran*³³ has described a column (Fig. 37) for general laboratory use, suitable for esterification, drying, or fractionation, which simulates commercial units. Its over-all height (including three-necked flask, column, and dephlegmator) was approximately 111 cm. (44 in.). The column was insulated by asbestos rope held in place by a wrapping of tape and was filled with glass beads or coarse carborundum to a point where the constriction in its larger diameter began. If packing was allowed in the

upper section, flooding resulted. The dephlegmator was unique in that it was built on to the column by split-rubber stoppers and pyroxylin sheeting. The lower rubber stopper, shown in the

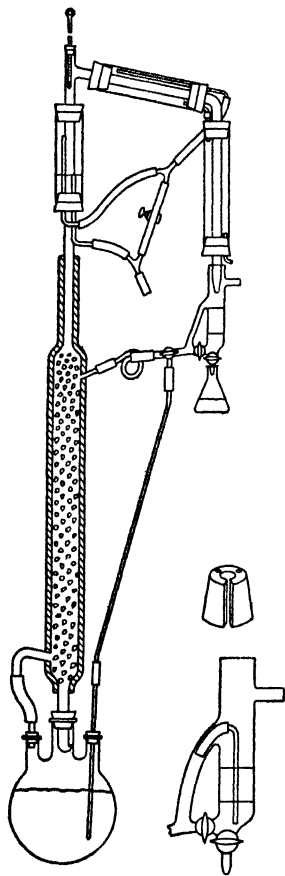


FIG. 37.—Fractionating column of Doran.

insert, had two holes for the customary water inlet and outlet lines and was slit so that it could be put around the tubing; the upper contained only one hole for an air vent. A piece of medium-thick pyroxylin sheeting, cut to the desired size, was first rolled to the diameter wanted, tied in this position with a string, and heated in an oven at 90° for one hour to set it in the rolled form. The rubber stoppers were then put in place, and the slits closed by binding with fine wire in two or three places. The pyroxylin shell was put in position and sealed by pouring acetone between the overlapping surfaces and holding tightly in place for a few seconds. All joints were covered with a generous coating of duPont's household cement. The upper condenser was made in the same manner, except that no venthole was needed in the upper stopper, and the rubber stoppers could be moved over the tubing instead of being slit. With additional cost, this assembly could be simplified by use of ground-glass joints. The separator^{33a} was connected to the column through a circular trap, which was constructed from 1.6-mm. capillary tubing with an

outer diameter of 6.3 mm. When the still was operated for esterifications with constant-boiling mixtures, the separator was filled until the benzene or other water carrier overflowed through the return line to the column or flask. The water was drawn off through the bottom. Should the carrier liquid be heavier than water, *e.g.*, carbon tetrachloride, the lower layer

could be returned by inserting a siphon made from a small-bore L-shaped glass piece with rubber tubing which fitted snugly but not tightly into the upper return arm. The siphon was primed by allowing the receiver to fill beyond the upper outlet. Reflux in the fractionating column was controlled by either varying the amount of water that flowed through the dephlegmator or sliding the outlet tube up or down.

84. From the standpoint of size, care in construction, and efficiency the column constructed by *Fenske, Quiggle, and Tongberg*⁷ deserves special mention. It was made from $\frac{3}{4}$ -in. brass pipe 52 ft. long, packed with alternate $\frac{1}{2}$ -in. sections of $\frac{1}{4}$ -in. glass rings and 1-in. sections of No. 24 Lucuo wire helices, thus reducing channeling by variations in the free space of the two packings. A 2-in. thickness of 85 per cent magnesia pipe lagging was placed over the pipe; and chromel resistance ribbon, $\frac{3}{8}$ in. wide by 35 Brown and Sharpe gauge, was then wound over this lagging. Another 1-in. layer of magnesia was then applied on the outside. The chromel ribbon was wound in three sections so that temperatures at the top, middle, and bottom of the column could be controlled independently. Thermocouples were placed in the winding at the same height as couples in the column, so that the jacket temperatures could be brought up to those inside. The head of the column was also wound and similarly controlled. In absence of visual observation, the reflux ratio was determined by measuring the temperature rise of the condenser water and calculating from the heat of vaporization of gasoline the amount condensed. Flow of water was made constant by means of an overflow reservoir and proper control valves. Thermocouples measured the temperatures of inlet and outlet lines. All of the liquid being distilled was condensed, but only a part was withdrawn as product. In general, a reflux ratio of 30:1 was established. The holdup of the column was about 50 ml. of hot liquid. The still—a metal one—contained 5 l. and was heated electrically. To secure better heat distribution through the liquid, copper fins were brazed to the bottom. To allow for expansion of the column when heated, the still was connected to the column through a section of $\frac{3}{4}$ -in. flexible Seamlex metal tubing. A manometer connected to the still showed a rise in pressure when flooding occurred. Because

of the height of the column (the sections were silver soldered together) the liquid was refluxed for several hours, to bring out equilibrium conditions and to concentrate the lowest boiling material in the head, before the take-off line was opened. Efficiency of this column may be judged from results with the two isomers of diisobutylene made from tertiary butyl alcohol by treatment with 50 per cent sulfuric acid. The crude product, freed from isobutene and distilled once to separate triisobutylene, was distilled through the column. From 4,500 ml. of material, 2,4,4-trimethyl-1-pentene (b.p. 100°) and 2,4,4-trimethyl-2-pentene (b.p. $103.4^{\circ}/737$ mm.) were separated in the ratio of 4 parts: 1.

Columns of over 100 theoretical plates are described by Fenske, Tongberg, Quiggle, and Cryder.³⁴ They are advantageous in distilling petroleum. An enrichment factor, *i.e.*, the molal ratio of the components in the distillate divided by their molal ratio in the still when operating under total reflux, does not follow a linear change with increase in number of plates, as can be seen from the fact that increasing the plates from 30 to 100 caused a change of this factor from 19 to 13,780.

85. An excellent column with Fenske packing was used by *Kistiakowsky and coworkers*¹⁰ (see also Sec. 74) for the separation of isomers of butene. It was constructed of glass tubing 5 m. high and 18 mm. in diameter. Packing consisted of glass spirals of not less than three-quarters and not more than one and a half turns. The column was surrounded with a double-walled glass jacket through which cold alcohol circulated. The jacket temperature at the top did not differ from that of the condensing vapor by more than a few tenths of a degree. The dephlegmator was of the partial-condensation type. The glass still pot, contained in a Dewar flask, was heated by vapors of carbon tetrachloride, boiled by means of a coil of bare nichrome wire immersed in it. Approximately 2,100 g. of crude butene was used for a single charge. The boiling points of the two isomers separated were 0.96 and 3.73°C .

86. *Laufin, Nash, and Whitmore*³⁵ describe a column for general laboratory use filled with single-turn glass spirals. The packed section was 135 by 1.4 cm. and had an outer glass

jacket *G* (see Fig. 38) around which was wound resistance ribbon. An outer glass tube *H* provided insulation. Both jackets were held in place by asbestos tape. The resistance was in three equal sections, each with its own rheostat and thermometer next to the packed tube. The three heating elements with their rheostats were connected in parallel to a 110-volt lighting circuit, which was controlled by a fourth rheostat. Reflux was controlled by means of the sealed-in glass condenser well *A*, which was filled with glycerol or other suitable liquid in which was immersed a closely fitting copper condenser which could be raised or lowered by a screw suspension device. Outside the condenser *A* was wrapped resistance ribbon insulated by asbestos tape for use with high-boiling liquids. The thermometer was of the Anschutz type and was supported by a wire in the stopper. Below the thermometer was a centering device *F* to insure that reflux entered the center of the column. Packed section and head were enclosed in a wooden case with a removable glass front, and the whole was mounted in a frame so as to be portable. The column was checked with a spirit level before use to insure perpendicularity. It was equivalent to 23 theoretical plates and had an H.E.T.P. equal to 5.9 cm. (2.3 in.) as determined by a mixture of carbon tetrachloride and benzene. It could be used under reduced as well as at atmospheric pressures.

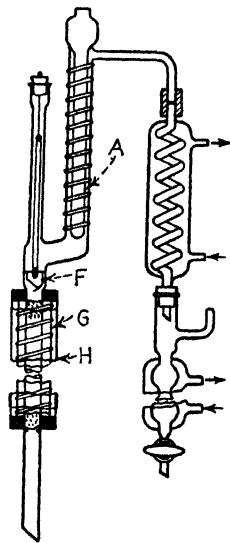


FIG. 38.—Fractionating column of Lauflin, Nash, and Whitmore.

87. Bubble-cap columns have not been previously described in this chapter, owing to their greater difficulty of construction and larger holdup, features that obviously make them less desirable in an organic laboratory. Yet the columns of Bruun²² deserve special mention because of their compact design. In the latest model the length from one theoretical plate to another is as small as 2 cm. Hence columns of 100 theoretical plates can be built within the confines of an ordinary laboratory.

Specifications are somewhat rigid, and the original article should be consulted for full details. Clarke and Rahrs³⁶ have designed a novel and very useful bubble-cap column.

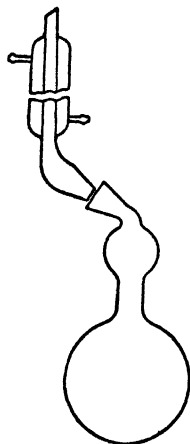


FIG. 39.—Apparatus of Stout and Schuette for quick conversion of reflux to distillation.

88. *Special distillation apparatus* is in many cases very desirable. Stout and Schuette³⁷ found the device shown in Fig. 39 very convenient for a quick change from refluxing to distilling. Brunjes and Furnas³⁸ merely tilted a flask at different angles (see Fig. 40). Any type of total-condensation variable take-off still head (see Sec. 79) is also adaptable to this purpose.

A number of columns especially designed for analysis have been described. Cooper and Fasce³⁹ employed a vacuum-jacketed Vigreux column 7 mm. inside diameter by 36 cm. long. Asbestos tape and No. 30 chromel wire were wrapped about the jacket. The still head was of the partial-condensation type, water being circulated through the dephlegmator for liquids boiling below and air for those boiling above 100°C. The section of tubing holding the thermometer was also glass-jacketed, and the 5-ml. receiver was a water-jacketed burette. Wrapped column and dephlegmator were further enclosed in a wooden box packed with Kieselguhr and fitted with a window for viewing drops of reflux. Excellent results were obtained by 30- to 90-min. fractionation of 10 ml. of mixtures boiling 15° apart. Weston⁴⁰ used a column of very nearly the same dimensions and construction but with a still head of the total-condensation variable take-off type. When a mixture of 5 ml. each of 1- and 2-chlorobutene boiling about 10° apart was distilled, 4.2 ml. of low-boiling and 3 ml. of high-boiling isomers

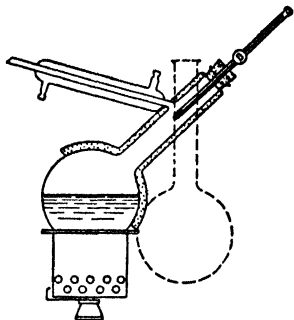


FIG. 40.—Brunjes and Furnas's tilting flask for changing from reflux to distillation.

were obtained. The remainder was consumed, partly (2.3 ml.) in changing from the low to the high temperature level and partly

(0.5 ml.) in holdup. Any column constructed with due attention to packing and insulation becomes an analytical column whose capacity for separating mixtures is limited only by its height and the operator's skill.

Frequently, it is necessary to distill in a dry or inert atmosphere. In such cases a receiver of the type used by Schlesinger

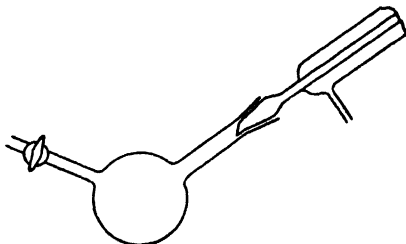


FIG. 41.—Schlesinger and Martin's receiver for use with a dry or inert atmosphere.

and Martin,⁴¹ shown in Fig. 41, becomes useful. Other receivers used in vacuum distillations (see Sec. 96) are adaptable to such operations.

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CHAPTER V

VACUUM DISTILLATION

89. Vacuum distillation plays an important role in purifying and isolating organic compounds. Use of very low pressures has often been instrumental in increasing the quantity of product from a reaction. For example, Späth and Lederer¹ found that the yield of 3-[β -aminoethyl]-indol from reaction of phenylhydrazine with *n*-butyraldehydediethylacetal was increased from 45 to 75 per cent when purification of the crude material was carried out by vacuum distillation (0.3 to 0.01 mm.) rather than by crystallization.

Vapor pressure varies logarithmically as the inverse of the absolute temperature. Hickman² has collected data, shown in tabular form below, that portray the advantages of distillation at low pressures, particularly if the compound is decomposed

TABLE 34.—CHANGE OF BOILING POINT WITH PRESSURE

Water		Ethylene glycol		An average compound	
V.p., mm.	B.p., °C.	V.p., mm.	B.p., °C.	V.p., mm.	B.p., °C.
760	100	760	200	760	About 350
526	90	10	80	0.10	160–210
4.6	0	0.1	20	0.01	100–130
0.034	–50	0.001	40–60

easily when heated. Unsuspected factors often combine to defeat realization of such benefits. Size and position of side arm, type of receiver, method of producing the vacuum, all are matters of greatest importance. These subjects as well as many others relating to the problem of producing and maintaining satisfactory vacuum conditions will be discussed at some length in succeeding pages.

90. Size and Position of Side Arm.—For pressures down to 15 mm. the ordinary distillation flask is satisfactory. When the pressure is reduced below this level, and particularly when it is as low as 2 mm. or less, the size and position of the side arm attain great significance. As Hickman² points out, an experimenter may go to great lengths to produce a vacuum less than a micron, yet fail to benefit properly from his efforts because the pressure necessary to drive vapors from distilling surface through neck and side arm is from 1 to 4 mm. Assume, for example, that vapor is arising from a liquid surface 10 cm. in diameter at a rate of 10 cm. per second in the flask. If the neck has a diameter of 2 cm., the vapor velocity in that section will be increased of 250 cm. per second. When it passes through the 5-mm. side arm, its velocity becomes 4 m. per second. Most of the pressure difference arises from the small diameter of the side arm. If we assume a 20-cm. length for this section, the pressure necessary to drive vapors from flask to condenser at a rate that will produce a drop every 6 to 8 sec. (0.4 g. per minute) with a liquid whose average molecular weight is 200 and boiling temperature 150° can be approximated by means of the equation

$$\Delta p = \frac{V128\eta L}{\pi D^4}$$

where Δp = the pressure in dynes per square centimeter between entering and issuing gas.

V = the volume of gas in cubic centimeters per second at pressure p equal in this case to 780.

D = the diameter of the side arm in centimeters.

L = the length of the side arm in centimeters.

η = the viscosity of the gas, assumed to be 1.7×10^{-4} .

Substituting in the preceding equation and inserting proper factors for conversion of dynes to millimeters of mercury, we obtain

$$\Delta p = \frac{780 \times 128 \times 1.7 \times 10^{-4} \times 20 \times 750}{3.1416 \times 0.5^4 \times 1.013 \times 10^6} = 1.14$$

This result means that at a relatively slow rate of distillation there will be a pressure of 1.14 mm. inside the flask which is additional to that measured at the receiver. The condition is

much worse with a 4-mm. side arm, in which case, for the same number of drops, the pressure would have to be at least 8 mm. Side arms of even smaller diameter are indeed common in the laboratory. It is obvious that a technician may go to great trouble in getting a vacuum of less than a millimeter at the receiver and not be aware that the construction of the flask makes it impossible for him ever to obtain a vacuum better than 6 to 10 mm. on the surface of the boiling liquid where it is most needed.

Height of side arm on the neck is also of importance at very low pressures, since some constriction occurs in the neck itself. This pressure effect can be translated into temperature by reference to observations of Krafft³ that ethyl stearate had a boiling point (thermometer immersed in the liquid)

of 154° when the side-arm outlet was 65 mm. above the boiling surface and only 139° when the distance was shortened to 25 mm., although the pressure in the receiver in both instances was approximately 0.001 mm. Similar differences in temperature with variation in side-arm position were observed with ethyl palmitate, ethyl myristate, and ethyl laurate.

They are due⁴ to the pressure necessary to drive vapor to the increased height above the liquid surface. The effect will be noticeable only with substances of large molecular weight under very low pressures. In construction of flasks for distilling large molecules which are apt to be decomposed by heat, it is therefore necessary to have large outlets placed as near the distilling

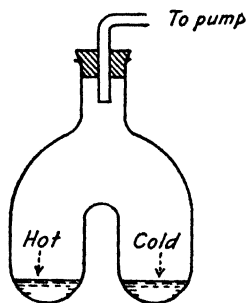


FIG. 43.—Vacuum-distillation apparatus with a short path to condenser.

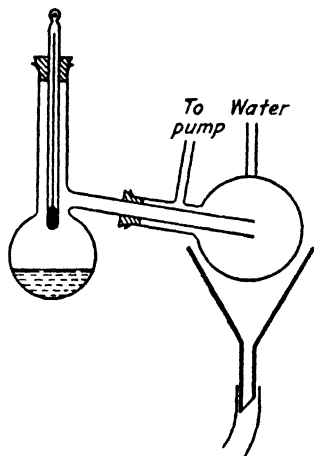


FIG. 42.—Vacuum-distillation flask with wide side arm.

surface as possible. Illustrations of such apparatus are given in Figs. 42 and 43. In the former the conventional side arm is replaced by a tube of larger diameter sealed into the neck directly

above the bulb; in the latter a section of large tubing is bent into an inverted U shape so that vapors need pass by a very short path to the condenser. Tilting the former apparatus also reduces the distance to the outlet. In both types the danger of having the charge bump into the receiver may be averted largely by filling the distillation compartment with glass wool to a height slightly above the surface of the liquid being distilled (see Sec. 92).

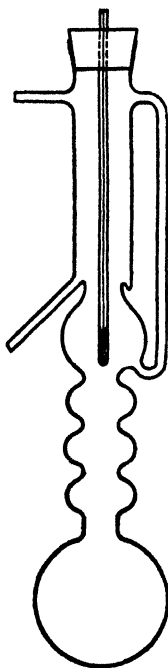


FIG. 44.—
Hickman automanometer still.

Another method of avoiding pressure drop through the side arm of a flask is to condense in the neck and allow the condensate to run out through the side arm. This construction is the same as that employed in the total-condensation variable take-off still heads in fractionating columns (Sec. 79). Hickman² has presented data to show results with such a column in observing correct temperatures. His apparatus (Fig. 44) has the additional feature of having a manometer tube at the point where temperature is being measured. The manometer fluid is the condensate itself, and the difference in height between the two arms of this "automanometer" are added, with suitable allowance for specific gravity, etc., to the pressure reading usually made at the receiver. By making this correction in addition to eliminating the side-arm effect the true temperatures of the vapor above the boiling liquid may be obtained. Figure 45 shows the differences in results obtained with the "automanometer" still and with an ordinary flask having a 5-mm. internal diameter side arm. With the former the logarithm of pressure plotted against temperature gives a straight line. With the latter a considerable divergence occurs at pressures below 10 mm. The difference is greater as the heat input is increased from 40 to 60 watts. That is to say, a difference in distillation rate under vacuum in an ordinary flask with a 5-mm. side arm at pressures below 15 mm. will result in changes in the boiling point of the liquid being distilled. Is it any wonder that it is often difficult to reproduce published results at very low pressures?

91. Stoppers.—All stoppers in a vacuum assembly must be tight. Rubber stoppers, while most desirable from the standpoint of insurance against leaks, are often attacked by hot organic vapors. Cork stoppers, if well rolled and bored with a sharp borer, are frequently satisfactory. If the outside of a cork stopper, previously softened by rolling, is burned by turning it in a flame for a short time, a great improvement is realized. A stopper so treated may sometimes function in a suitable manner even when the pressure is below 1 mm. Various smears, waxes,

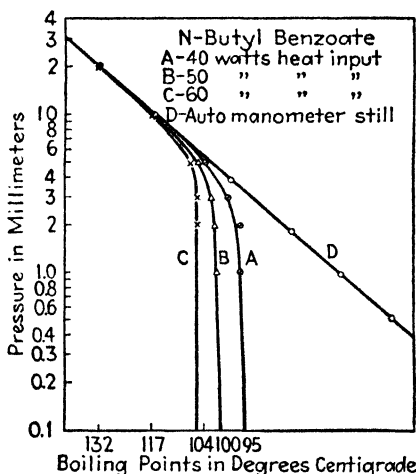


FIG. 45.—Effect of pressure at different rates of distillation on the boiling temperature of *n*-butyl benzoate in an ordinary still.

glue, and the like are often employed as aids in obtaining a good vacuum. If the cork stopper is well rolled and cut with a freshly sharpened borer, and particularly if it has been burned before use, there is usually no excuse for smearing the joints with such materials. If some concession for deficiencies of man or materials must be made, recourse can be had to paraffin or other wax applied while the apparatus is under suction. Some of the commercial household cements, purchasable at any hardware store, are satisfactory. The handles of tooth brushes that have been made from a plastic can be dissolved in amyl acetate or other lacquer solvent and used to advantage. For corks exposed to a very high temperature, a varnish base, obtained as residue

by distilling the solvent from a commercial varnish,⁵ can be applied. The surface of such a smear becomes covered with a thick scum, while the underside remains soft so that cracks are filled as soon as they appear. Some protection from hot organic vapors may be had by covering them with glue. Peters and Baker⁶ found that stoppers so impregnated lasted for 10 hr. with temperatures reaching as high as 350°. Vivian and Reid⁷ found that rubber stoppers which would have been attacked by hot vapors of sulfonic acids were protected by coating with sodium silicate.

92. Bumping.—One of the most annoying occurrences in vacuum distillation is bumping. Fortunately it may be entirely prevented by the simple expedient of packing enough glass wool⁸ into the flask to rise about 4 to 5 mm. above the surface of the liquid. An oil bath is preferred as the source of heat. With these two conditions fulfilled even the most viscous mixtures distill smoothly. The method is far superior to other methods in convenience and adaptability. Asbestos has also been used in place of glass wool, particularly in distilling micro quantities in tubes. Many other suggestions have been recorded. Ebullator tubes, *i.e.*, capillary tubes closed at one end and inverted in the liquid, glass beads, pieces of pumice or tile, and currents of air bubbled in through a capillary are common devices which are often satisfactory but less effective than glass wool. Chemical compounds⁹ such as sodium bicarbonate that decompose during distillation are useful. The bottom of the flask may be sandblasted,¹⁰ coated with silica gel baked at a high temperature,¹¹ or covered with powdered glass fused¹² over the lower half in order to increase surface area and thereby make ebullition of vapors more even. A metal wire¹³ sealed through the bottom of the flask conducts heat into the liquid so that distillation is more regular. Variations in heating, as secured by a ring burner,¹⁴ an inner heating coil, or induced electrical currents have been employed. A way has even been found for rotating the flask¹⁵ during distillation. All of these devices as well as others serve to break up the superheated zone of liquid so that sudden ebullition of a large body of material is avoided. A method that minimizes the effect of bumping is to insert through the cork a long glass rod which terminates in a horizontal position above

the surface of the liquid being distilled, the flask being in an inclined position.¹⁶ The rod acts as a baffle which retards the ascending liquid. The latter seems to fold over the rod and strike the top of the flask at an angle. Breakage from violent bumping is thereby avoided. Still another method is to make indentations,¹⁷ similar to those in a Vigreux fractionating column, from the top toward the bottom of the bulb so that the sharp points break up the large liquid film.

As stated before, the proper use of glass wool will effectively and simply handle all ordinary problems of bumping that arise in the laboratory. It has, moreover, the advantage that the boiling point of the compound is not lowered as is the case when a current of air or gas from decomposing chemicals is employed.¹⁸ Use of such measures as the latter is, indeed, equivalent to employing codistillation (see Sec. 120), and the boiling point will necessarily be lowered by an amount proportional to the quantity of air sucked through the liquid, making fractionation less efficient and results less reproducible.

93. Manostats.—Regulators for automatic control of pressure have become exceedingly numerous within the last few years. It is impossible to discuss all of them within the short space allowed in this volume. In general, a manostat keeps the pressure constant by allowing intermittent operation of pump or by admitting air through a controlled leak. In the former class the manostat is set to turn the pump on or off as the pressure oscillates about the desired level. In the latter it operates a flutter valve which bleeds in small quantities of air as needed. Intermittent pump operation is convenient when distillations must be carried out in an inert atmosphere. It also has an advantage in that audible warning of minor leaks is given by too frequent starting of the pump. A system that has been carefully set up should require only occasional pumping. A flutter valve, on the other hand, is independent of the method of obtaining a vacuum and, where a motor-driven pump is used, avoids the wear attendant in many cases with frequent starting and stopping.

Intermittent pump operation is made possible with an arrangement of Huntress and Hershberg,¹⁹ outlined in Fig. 46, for controlling, by means of a minute thermionic current, the heavy

starting load of the induction motor operating the pump. They employed as a manostat a U-type manometer with tungsten

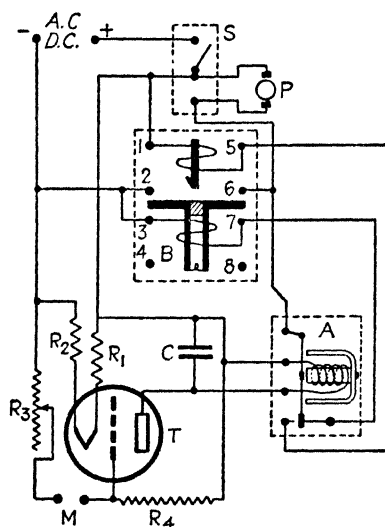


FIG. 46.—Wiring diagram for universal 110-volt thermionic relay, as described by Huntress and Hershberg.

A. Struthers Dunn, Inc., relay-type CXB-51, coil *H*. Coil resistance, 2,700 ohms. Coil rating, 2 milliamp. Contact rating, 2 amp. at 110 volts.

B. Struthers Dunn, Inc., relay-type CS600. Contact rating, 30 amp. Universal alternating or direct current. When assembling it is well to mount on sponge rubber to minimize noise.

C. 4-mf. condenser. Rating, 300 volts direct current, 125 volts alternating current.

M. Manostat contacts.

P. Pump motor, 0.125 to 1 hp. The rated operating current is usually much less than the starting current which must be broken at the contacts making necessary the auxiliary heavy-duty relay *B*.

*R*₁. 25-watt, 115-volt tungsten filament, General Electric Mazda lamp.

*R*₂. 40-watt, 115-volt tungsten filament, General Electric Mazda lamp.

*R*₃. Variable series resistor, 25,000 to 250,000 ohms range. This resistor serves as a fine adjustment to compensate for unavoidable variations in lamps *R*₁ and *R*₂ and in grid leak *R*₄. In practice this is adjusted to the highest resistance (and hence the smallest operating current) that will give dependable operation.

*R*₄. Grid leak, 8 megohms.

S. Single-pole flush-tumbler switch and plug receptacle for pump motor.

T. 71-A type tube, 5-volt filament. The filament should operate at a dull red heat with lamps *R*₁ and *R*₂ of the recommended rating.

contacts on the open-arm side. It was mounted on a swivel so that the position of the mercury in the tube could be changed by tipping the manostat. The apparatus is very compact and

simple and operates on either direct or alternating current. Its range is limited by the length of the two manometer-like arms.

94. With *flutter-valve control*, air is let in intermittently through a capillary tube connected to the system. The open end is

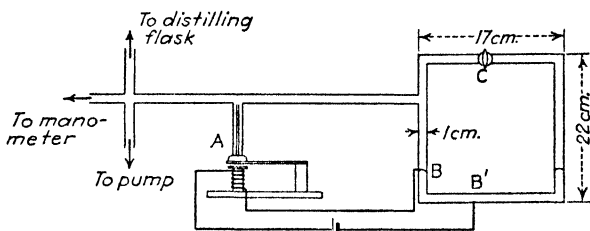


FIG. 47.—Manostat operating a flutter valve, as described by McConnell.

automatically closed by a stopper when the desired amount of air has passed and opened again when the vacuum becomes too low. A simple form, described by McConnell,²⁰ is shown in Fig. 47. The manostat is a circuit of glass tubing with a stopcock *C* at the top and platinum contacts *B* and *B'*. When the system has been evacuated to the desired level, as shown by the manometer, the stopcock *C* is turned. Mercury rises on one side and touches contact *B* which closes the circuit through the relay. The relay, in turn, pulls the armature away from the capillary opening *A* so that air is admitted. The mercury then falls away from the contact, thus opening the circuit in the relay, etc. The manostat stopcock must fit tightly to prevent leakage into the right side.

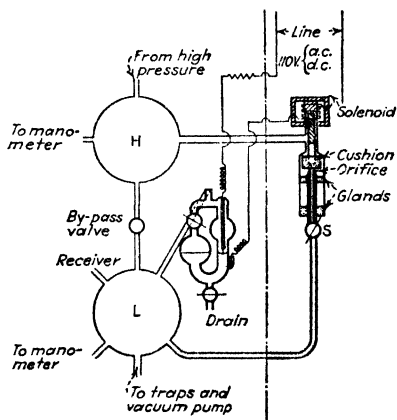


FIG. 48.—Flutter valve of Jacobs with sulfuric acid manostat of Hershberg and Huntress.

Gravity instead of a spring is used to close the valve in the design of Jacobs.²¹ The parts, shown schematically in Fig. 48 in conjunction with appurtenances, are enumerated below.

Cushion.—A No. 0 rubber stopper half bored, boiled in alkali, and fitted on to the end of a glass tube containing the armature.

Armature.—A 4- to 5-mm. iron rod 3 cm. in length, slotted longitudinally and circumferentially to reduce eddy currents. To avoid corrosion it is enclosed in a thin-walled glass tube which, in turn, slides up and down in a glass tube.

Solenoid.—A standard unit, in this case CX 1388, made by the Struthers Dunn Company of Philadelphia. The solenoid is operated from a 110-volt alternating- or direct-current line in series with the sulfuric acid monostat of Hershberg and Huntress²² and a 25-watt lamp. Use of a solenoid obviates the necessity for a relay.

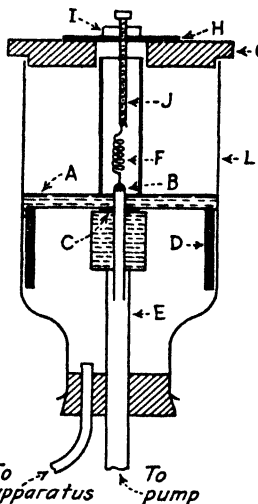


FIG. 49.—Spring-tension manostat of Liebig.

A unique flutter valve which operates from a spring-tension manostat instead of an electric magnet is described by Liebig.²³ The bottom of a wide-mouth bottle *L* (see Fig. 49) is cut off, and the edges smoothed by rubbing with emery cloth. It is then fitted with the following parts:

A copper cylinder *D* made from a sheet of 1.7-mm. copper.

A rubber disk *A* cut from a No. 14 rubber stopper so that it fits snugly inside the bottle *L* and upon the copper cylinder *D*.

A brass rod *B* with a hook on the upper end for attachment to the spring; a brass washer *C* soldered firmly to the rod to prevent its slipping through the rubber disk; and a section of heavy-walled pressure tubing, 0.125 in., with its ends cut smoothly and perpendicularly to the hole. The lower end of the rod reaches into the glass tubing *E*.

A spring *F* whose tension can be varied by the threaded rod *J*, held in place by the lock nut *I*, is supported by the wooden cover *G* and the metal plate *H*. The strength of this spring obviously regulates sensitivity. Lines leading to the apparatus and the vacuum pass out through the stopper

Glands.—Two slices of a one-hole rubber stopper to hold the capillary in position.

Stopcock *S*.—A device to get better regulation of the leak.

High-pressure Reservoir *H*.—A large flask from which air is let into the capillary. By keeping the air in this reservoir at a pressure just slightly higher than is desired in the distillation system, the sensitiveness of the apparatus is increased. This reservoir may also be used in cases where an inert gas must be admitted.

Low-pressure Reservoir *L*.—A constant-pressure reservoir which serves to minimize changes in pressure that occur in the distillation system. Receiver, sulfuric acid manostat, and pump are connected to this reservoir.

closing the neck of the bottle. The operation of the regulator is obvious from the drawing.

Palkin and Nelson²⁴ have described another apparatus which combines the flutter-valve arrangement with intermittent pump operation. Relay and flutter valve are mounted inside a large flask or bottle which is, in turn, kept at a pressure 4 to 30 mm. from that in the distillation system. Two manostats are needed, one to control pressure in the reservoir containing the flutter valve by intermittent operation of the pump, and the other to regulate admission of air through the flutter valve. The dual system combines the advantages of intermittent pump operation with those of the flutter-valve type. Schierholtz²⁵ devised an ingenious balanced-beam manostat in which the shift of mercury from one side to the other with pressure changes actuates a make-and-break contact. In the apparatus of Swayze^{26a} the rise and fall of a float in the open end of a manometer tube operate a nitrogen-filled mercury switch.

Attention should also be directed to the apparatus perfected by Emerson and Woodward^{26b} by which constant pressure is maintained by means of a leak through a mercury trap.

95. Sensitiveness of a manostat can be greatly increased by use of a liquid lighter than mercury. Sulfuric acid (sp. gr. 1.71) has been found by Hershberg and Huntress²² to be admirably suited for this purpose. This liquid has about one-seventh the density of mercury, has good conductance, and wets the sides of the glass. Since it is about fifteen times as viscous as the metal, the diameter of the tube must be approximately four times that used for mercury if corresponding sensitivity is to be obtained. Owing to the presence of dissolved gases, the filled manostat should be evacuated to a pressure of 0.1 mm., boiled gently for 5 min., and then cooled under vacuum. When not in use, it should be kept under vacuum by closing a protective stopcock. Sulfuric acid of specific gravity 1.84 slowly evolves gases under vacuum and is therefore not suited for use as a manostat fluid.

96. Receivers.—A large number of receivers have been designed for collecting fractions without breaking a vacuum in the distilling apparatus. They may be classified broadly into the triangle and the rotating receiver types. The *triangle*

type, originally proposed by Thorne,²⁷ is illustrated in Fig. 50. By obvious manipulation of stopcocks (screw clamps and pressure tubing may be used instead) the flask at the bottom may be replaced without interrupting the distillation. Many varieties of this form are possible. Bogert²⁸ has graduated the

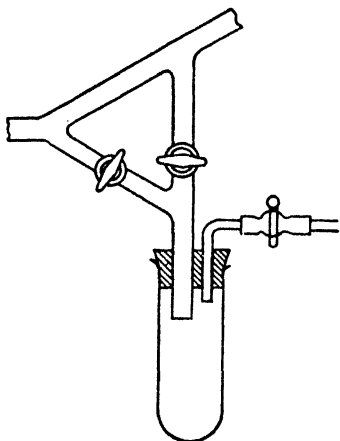


FIG. 50.—Triangle-type receiver of Thorne.

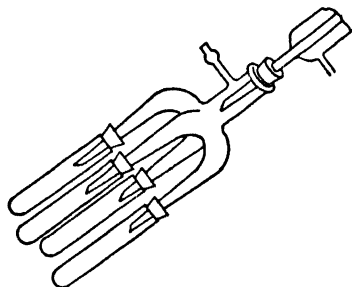


FIG. 51.—Inclined rotating receiver.

vertical arm so that the volumes may be read as collected. Lorang and Kluizenaar²⁹ have made an exceedingly compact arrangement in which all stopcocks are concentrated into one.

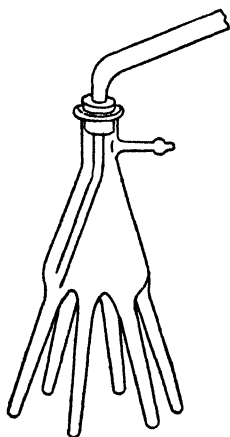


FIG. 52.—Modified Pauly receiver made from an Erlenmeyer flask.

The *rotating-receiver* type collects fractions in separate containers by revolving them in turn under the delivery tube of the condenser. This form has the advantage that sharper cuts can be made. Gerboff and Kessler³⁰ employed a vacuum desiccator containing a revolving table. Simple star arrangements³¹ with three, four, or more points are the most useful and satisfactory forms. They may be attached in either a vertical or an inclined position, as shown in Fig. 51. In the former case the delivery tube must be bent in order to direct the distillate into the desired receiver. Erlenmeyer

flasks (250 ml.), preferably with an outward bulge at the bottom, are often adapted³² to construction of this type. A vertical

arrangement³³ with six outlets is shown in Fig. 52. The openings in the flask must be equally spaced from the center and should be at least 12 mm. in diameter to provide easy access of condensate. There will be no spattering at the end of the adaptor if the latter is 8 mm. or more in diameter. An inclined form³⁴ is shown in Fig. 53. Six outlets, 10 by 40 mm., are attached at equal distances around the periphery of the base. The receivers are 50-ml. Erlenmeyer flasks with a 90-deg. bend at the neck.

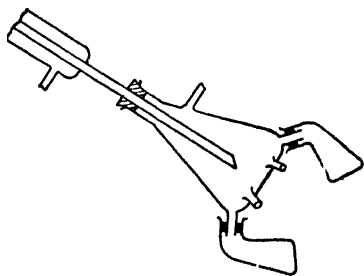


FIG. 53.—Rotating receiver made from an Erlenmeyer flask.

A novel and useful apparatus has been made by Ellis³⁵ (Fig. 54). Drops fall from the condenser into a small cup attached to a capillary tube. The latter conducts the liquid to a vertical larger tube so that it falls against a bent-glass rod or closed tube which can be rotated in a greased pressure-tubing bearing to deliver the drops into separate

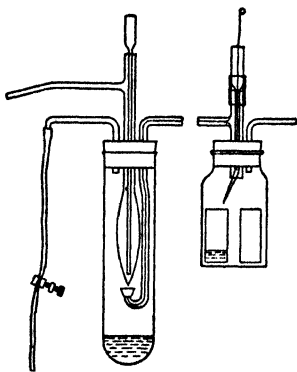


FIG. 54.—Receiver of Ellis.

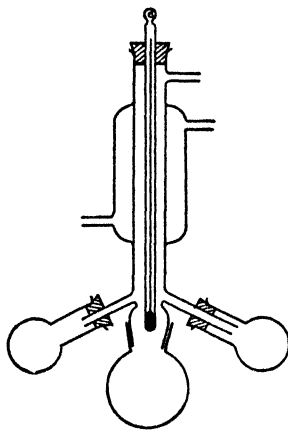


FIG. 55.—Flask with multiple side arms.

receptacles. In the absence of evolved gases necessary to force the drops through the capillary a small amount of air may be let in through the opening on the left. For solids that melt at low temperatures a heating element is wrapped about the tube. The

whole arrangement can be adapted to distillations in a flask. With proper precautions against bumping the receiver can be set very close to the surface of the distilling liquid so that the advantages of a molecular distillation (see Sec. 103) can be realized.

Flasks with multiple side arms³⁶ (see Fig. 55) are sometimes convenient. The apparatus can be tipped at an angle of 20 deg. Though useful in special cases, it is subject to breakage and is troublesome to make.

97. Pumps.—Commercial *oil pumps* are available in most laboratories. Their efficiency depends on the vapor pressure of the oil which obviously is lowered if volatile organic liquids are not trapped. Moreover, traps are necessary to catch gum-forming aldehydes and corrosive vapors which ruin the mechanism. The trap may be a container cooled with a freezing mixture, care being taken that the inlet tube is very large so that condensed vapors, if frozen, will not plug the line. Columns of glass beads or of short pieces of tubing wet with sulfuric acid, solid absorbents such as activated alumina, soda lime, or carbon depending on the nature of the material being absorbed are also suitable as trapping agents. In the organic laboratory a good grade of crankcase oil is usually satisfactory for the pump.

98. Condensation pumps not only produce a better vacuum but also increase the capacity. According to Hickman,² a small rotary oil pump will evacuate to $4\ \mu$ at a uniform rate of about 100 ml. per second. When the same pump is backed by a mercury condensation pump of jet diameter 1.5 cm. the rate is increased to 5,000 ml. per second at $4\ \mu$. Because of its long life,

TABLE 35.—PRESSURES OBTAINED WITH SOME ORGANIC LIQUIDS IN A CONDENSATION PUMP

Compound	B.p. at 1 mm.	Lowest pressure, mm. of Hg at 25°C.	
		Without a trap	With an ice-cold trap
<i>n</i> -Butyl phthalate.....	149	2×10^{-4}	2.0×10^{-6}
<i>n</i> -Amyl phthalate (Amoil).....	164	2.5×10^{-5}	5.0×10^{-7}
<i>n</i> -Octyl phthalate.....	211	5.0×10^{-6}	5.0×10^{-8}
2-Ethylhexyl phthalate (Octoil)...	184 (approx.)	5.0×10^{-7}	5.0×10^{-8}

freedom from dissolved gases, and thermal stability, mercury is the best liquid to use for most purposes in the laboratory. Without a trap, it is good only to 10 μ . Butyl phthalate has a vapor pressure one hundred times less than that of mercury at room temperature, but its use in ordinary laboratory processes is lessened by danger of contamination with organic liquids. Apiezon oil has a still lower vapor pressure. Table 35 gives the boiling points and attainable pressures of a number of organic liquids.³⁷

Kraus³⁸ and Munch³⁹ have designed a mercury-condensation pump for the laboratory which can be used with an ordinary water aspirator. Such an apparatus effects considerable economy, since the initial cost of the condensation pump is much less than that of commercial oil pumps. Neither is the former ruined by corrosive vapors. Condensable vapors can be pumped, and the mercury is easily cleaned. The important points to be considered in this pump are the return tube (see Fig. 56) which should be 14 cm. long and the small nozzle which should be 3 mm. in inside diameter and project a distance of 1 cm. into the narrow

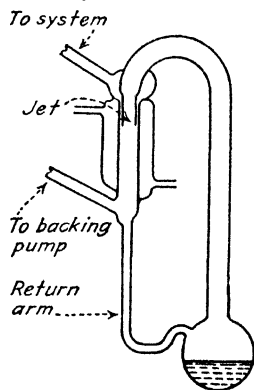


Fig. 56.—Mercury-condensation pump.

part of the condenser. The annular space between jet and condenser must be 0.5 mm. The boiler is a flattened bulb—a shape claimed to give rise to less bumping—about 5.5 to 6.5 cm. in diameter and 4.5 cm. in thickness containing mercury to a depth of about 1 cm. The upright arm leading to the nozzle can be made of 1.5-cm. tubing and should preferably be wound with asbestos and resistance wire. Fifty feet of No. 22 chromel wire requires no external resistance and facilitates operation of the pump. A 15-cm. condenser is long enough to condense the mercury. Usually, organic vapors must be trapped before they reach the pump inlet lest they be carbonized by the hot mercury. The water pump used in conjunction with this apparatus should produce a vacuum of 30 mm. or better. A safety trap must be used between mercury pump and aspirator. This apparatus has a wide use in the laboratory. It will produce a vacuum as low as

20 to 50 μ if the water pump is good and is therefore suitable for much low-pressure distillation. It can be employed with the flutter-valve arrangement to produce a constant vacuum in a system. Because of its increased capacity it is a great aid in hastening evaporation of large quantities of solvents or of water.

Although a mercury pump of the foregoing construction has the widest utility in the organic laboratory, pumps with larger jet diameter will have larger capacity. When backed up by an oil pump—large-capacity oil pumps give better results—they are most serviceable for very low vacuums of 1 μ or less. A mere enlargement of the type shown in Fig. 56, with a considerably shortened return tube, is quite satisfactory. Other forms of construction exist, however, which may be seen by consulting Dushman's⁴⁰ work, Hickman's^{2,37} publications, Copley and coworkers,⁴¹ and others.⁴²

99. Another method of obtaining low pressures in the laboratory is by use of a *water pump, carbon dioxide, and potassium hydroxide*.⁴³ The system is exhausted with the water pump and then filled with carbon dioxide. This process of exhaustion and filling is repeated four times, after which the apparatus is sealed off, and a stopcock, which connects to a bulb, containing 50 per cent potassium hydroxide solution is opened. The carbon dioxide is absorbed, and the vapor

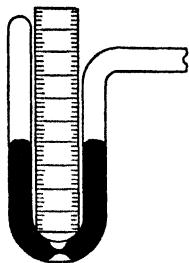


FIG. 57.—U-type manometer with constriction.

pressure of water is reduced by first cooling with ice and then with carbon dioxide snow. The bulb is then sealed off above the stopcock, and the distillation carried out in a closed system. Krafft claimed that he obtained a vacuum low enough to produce the green cathode rays in an electric discharge within 15 to 30 min. even in large containers.

100. **Gauges.**—The simplest mercury gauge consists of a tube over 760 mm. in height inserted at one end into mercury. The height to which mercury rises when the open end is attached to a vacuum is subtracted from the reading of a standard barometer which may be of commercial or student construction.

Much better than the aforementioned gauge are the direct-reading U-type gauges (Fig. 57). One end of the U tube is

evacuated and closed, while the other end is connected to the apparatus. The difference in level of the two mercury columns is a direct measure of the pressure of the system. The closed end of the U tube may be of any length depending on the range of pressures desired. Frequently a capillary constriction is placed at the bottom of the U in order to retard the movement of mercury when the vacuum is suddenly released. This device subtracts from the sensitivity of the gauge toward slight variations in pressure but reduces the breakage risk. An excellent method of filling manometers has been described by Cameron.⁴⁴ The U tube with both arms open is cleaned with cleaning solution, washed with distilled water until free from acid, and dried. The two arms—one constricted at the position where it is to be sealed—are sealed to the side arm of a specially constructed flask as shown in Fig. 58. The flask is then attached to a vacuum, and the purified mercury distilled. The jet above the distilling flask acts as a condensation pump, but the condensate, instead of running back into the flask, drains into the evacuated tube, the walls of which should be torched during the entire operation in order to drive out all adsorbed gases. When sufficient mercury has collected in the tube, it is sealed off at the constricted section.

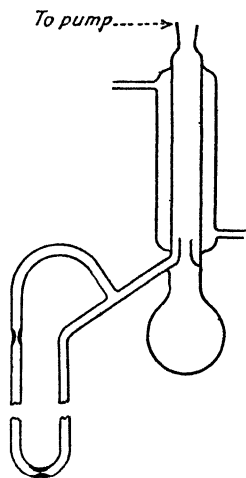


FIG. 58.—Cameron's device for filling manometers.

Such gauges are suitable for all ordinary laboratory work. Where measurement to a tenth of a millimeter is needed, the metal may be replaced by a suitable oil or one of the phthalate esters with low vapor pressure or by sulfuric acid (sp. gr. 1.71). Sensitivity can be increased further by inclining the closed arm.

101. At very low pressures such as are achieved in molecular stills more accurate measurements are required. Some form of the *McLeod gauge* is usually employed in these cases. The principle on which it operates is that of compressing a known volume of the gas under vacuum into a small capillary, also of known size. The additional height of mercury in a parallel capillary gives the

pressure of the compressed gas, and the original pressure in the system can be computed from these three figures by means of Boyle's law. Thus, in Fig. 59a the reservoir of mercury has been raised until the metal is just about to trap the gases that are in the bulb *B*. This bulb is usually about 250 to 500 ml. capacity. Its volume, as well as that of the capillary above it, is accurately measured before being sealed on to the apparatus. In Fig. 59b the reservoir of mercury has been raised until the liquid in the

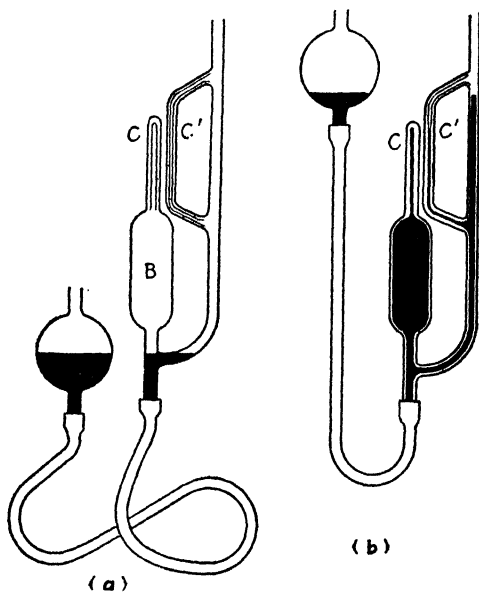


FIG. 59.—McLeod gauge.

capillary *C'* is level with the top of capillary *C*. The difference between the mercury levels in the two capillaries (the capillaries should be the same size and constructed from different sections of the same tubing) gives the additional pressure P_2 in millimeters of a volume V_2 of compressed gas in capillary *C*. The volume V_1 before compression is the combined volume of the bulb *B* and capillary *C*. The pressure in the system P_1 is then calculated by the equation $V_1/V_2 = (P_1 + P_2)/P_1$. It is customary to make the calculations for assumed pressures and prepare a direct-reading scale for use with these instruments. Other

methods of lifting the mercury are frequently preferred to the troublesome handling of the reservoir. Thus, a wooden plunger may be pushed down into the reservoir so that the mercury is forced up into the gauge. If the reservoir is under a vacuum such as is possible with a water pump, it is necessary only to bleed in a little air to lift the metal. The latter device permits a greatly shortened apparatus. Rotary-type⁴⁵ McLeod gauges have also been constructed. Gross and Wright⁴⁶ describe a simple gauge for pressures around 0.1 mm.

102. Fractionation under Vacuum.—Any of the columns described for fractionation at atmospheric pressure can be used in vacuum distillation. It is not possible, of course, to maintain a low temperature at the surface of the liquid if the column is very high, since pressure is required to force vapor through the column. The same considerations discussed in Sec. 90, on the size of the side arm, apply with equal force in this case. Greater velocity of vapors through the column may also make it more difficult to avoid flooding, particularly if the diameter of the packed section is small. With these limitations, it can be safely stated that fractionation is as possible at reduced as at ordinary pressures. An excellent example of the use of good fractionating columns for this purpose is found in the work of Peters and Baker,⁶ who separated a mixture of *o*- and *p*-ethylnitrobenzenes in a column 150 cm. high packed with 5- by 5-mm. glass rings and provided with an externally heated jacket. They claim as good separation in one distillation as is possible in 20 to 80 ordinary distillations with the same mixture. Lepkovsky, Feskov, and Evans⁴⁷ distilled 8.5 kg. of fatty acids from the hydrolysis of coconut oil, through a 1.8-m. (6-ft.) column 63.5 mm. (2.5 in.) in diameter filled with cut-glass tubing 5 to 8 mm. long by 3 to 4 mm. inside diameter. The column was lagged and electrically heated. A 12-l. flask was used, and low vacuum maintained by a mercury diffusion pump backed with an oil pump. A complete day was required for fractionation. The highest oil-bath temperature was 300°, and the temperature of the condensate varied from 79 to 176°. The temperature at the foot of the column varied from 180 to 260°. Very pure fractions consisting of caproic, 0.5 per cent; caprylic, 9.0 per cent; capric, 6.8 per cent; lauric, 46.4 per cent; myristic, 18.0 per cent; palmitic, 9.0 per cent;

stearic, 1.0 per cent; oleic, 7.6 per cent; and linoleic, 1.6 per cent were obtained. The methyl esters were also distilled. Gurin⁴⁸ fractionated mixtures of butyl esters of benzenesulfonylated amino acids using a mercury diffusion pump as the source of a vacuum.

103. The Molecular Still.—A molecular still may be defined as a still in which the distance between evaporating surface and condenser is less than the mean free path of the molecule. In an ordinary distillation a molecule leaves the surface of the liquid, collides with other molecules in the vapor state, and proceeds by devious paths to the condenser if, indeed, it escapes being knocked back into the liquid. In a molecular still the molecule goes in a straight path to the condenser. It is clear that in a molecular distillation the use of very low pressures is not alone sufficient. The condenser must be moved close enough to the evaporating surface so that escaping molecules are more apt to strike its cold surface than to hit other molecules. We can therefore say that a molecular still is one in which no recondensation occurs on the evaporating surface. The mean free path of air at various pressures is given in Table 36; that of large organic molecules is shorter. Obviously, the ordinary distillation apparatus has too great a distance between evaporating and condensing surfaces.

TABLE 36.—MEAN FREE PATH OF AIR AT VARIOUS PRESSURES

Pressure, Mm. Hg	Mean Free Path, Cm.
1.0	0.00562
0.1	0.0562
0.01	0.562
0.001	5.62

104. Langmuir⁴⁹ has supplied the equation

$$\eta = pS\sqrt{\frac{1}{2\pi MRT}}$$

by means of which the theoretical *rate of distillation* can be calculated. The number of mols of substance distilled per second η is related to the vapor pressure p at the evaporating surface, the effective area S of the evaporating surface, the molecular weight M , the gas constant R , and the absolute tempera-

ture T . As an example⁵⁰ a compound of average molecular weight 400 is distilled at a pressure of 0.001 mm. of mercury from a surface of 10 sq. cm. at 300°K. Substituting in the preceding equation, we have

$$\eta = 0.001 \times 1,333 \times 10 \sqrt{\frac{1}{2 \times 3.14 \times 8.32 \times 10^7 \times 400 \times 300}}$$

or 17×10^{-7} mol per second. This value is equivalent to 0.7 mg. per second. The actual rate is only about 10 per cent of that calculated, owing to reflection of molecules from the condensing surface. Lower temperatures in the receiver therefore increase the rate of distillation. It is also obvious that the presence of molecules easily volatilized reduces efficiency, since such compounds are apt to remain in the area above the liquid and hinder escape of less volatile molecules.

105. A number of *applications* of the still have been made. Washburn⁵⁰ distilled paraffin wax at 55° and cane sugar at 120°. Burch⁵¹ distilled petroleum fractions at temperatures of 112 to 314°. The fraction from 112 to 250° had an average molecular weight of 498; that from 250 to 314°, a molecular weight equal to 801; and the residue, a weight of 1,550. Freudenberg, Friedrich, and Bumann⁵² successfully distilled a tetrasaccharide at 265 to 290°. Carothers and Hill^{53*} applied it to the preparation of superpolyesters in which one component of a physical equilibrium was volatilized. Hill gives as the limit of application the point where the molecular cohesion on any molecule is greater than the heat of dissociation of the least stable bond. For example, $C_{70}H_{142}$ (molecular cohesion 70,800) can be distilled, while $C_{80}H_{162}$ (molecular cohesion 77,220) cannot. The value of the heat of dissociation of the carbon-carbon bond (about 75,000) lies

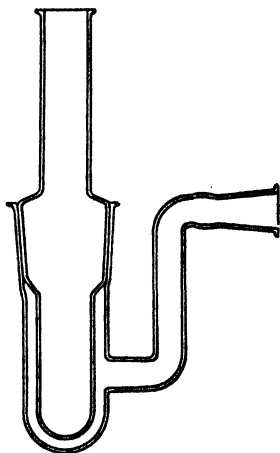


FIG. 60.—Molecular still for solids. Washburn type.

* These investigators, however, reported that heating in a stream of nitrogen sometimes accomplished the same result in shorter time.

between these two values. Watermann and Elsbach⁵⁴ distilled α -bromonaphthalene (b.p. $281^{\circ}/766$ mm.) at 18 to 20° when the pressure was a few thousandths of a millimeter.

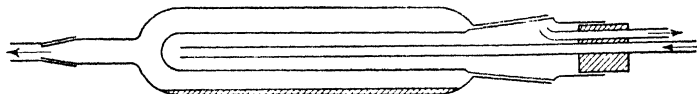


FIG. 61.—Freudenberg's quartz still for use with a cellulose derivative.

106. Only such *apparatus* will be described as can be taken apart easily and cleaned. Figure 60 shows an apparatus similar to one of the early forms used by Washburn but without a mercury seal on the ground joint. It is possible to dispense with mercury seals if a good grade of grease is used. The apparatus of Freudenberg and others was constructed of quartz and is illustrated in Fig. 61. The Hickman² alembic which is sold commercially is pictured in Fig. 62. This form gives very satisfactory results. With the aid of



FIG. 62.—Hickman molecular still for use with liquids.

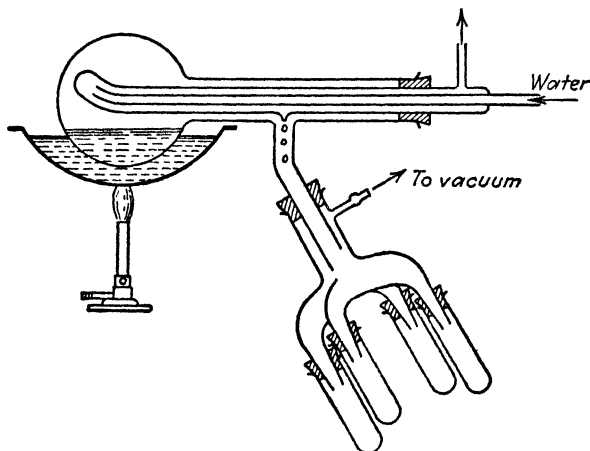


FIG. 63.—Horizontal-flask molecular still shown with bent-finger-type condenser, drip point and conventional four-point-star rotating receiver for collecting fractions.

interchangeable ground joints it can be fitted quickly into any assembly that is provided with corresponding parts. Watermann and Elsbach ran a tube through the bottom of the flask

to drain condensate to the receiver. The simplest still for liquids is a horizontal flask (Fig. 63). It can be constructed by students from common distilling flasks. Carothers and Hill used the tops of two vacuum desiccators (see Fig. 64) placed with their flanged edges together. Through the top, a flat-bottom condenser flask was supported. Through the bottom opening, a support for heating stand, resistance wires, and thermocouple was passed. Strain and Allen⁵⁵ utilized a commercial pyrex tubing having wide flanges in place of desiccator tops. The arrangement of Ellis³⁵ described in Sec. 96 can often be used. From natural materials such as cottonseed or cod-liver oil, Hickman² has removed the essential oils and waxes below 100°, the free fatty acids below 140°, free sterols and vitamins below 180°, and sterols and vitamin esters below 250°. Trilaurin, triolein, and other triglycerides are distillable at these low pressures.

107. In using a molecular still it is always advisable to test the apparatus before adding the compound to be distilled. Care must be taken with liquids to prevent sudden evolution of dissolved gases and low-boiling compounds. The vacuum must be applied gradually and maintained for some time before distilling. Warming, rotating, or tipping the flask on its ground-joint connection is frequently helpful in removing such trouble makers. The temperature of the vapor cannot be measured; that of the liquid can be determined if the construction permits a thermometer to be inserted. In many cases a thermocouple connected to the heating plate or a thermometer in the surrounding bath is the only means of approximating the temperature. Fractionation of compounds boiling near to each other is of course impossible, but separations can be effected if boiling points are far enough apart.

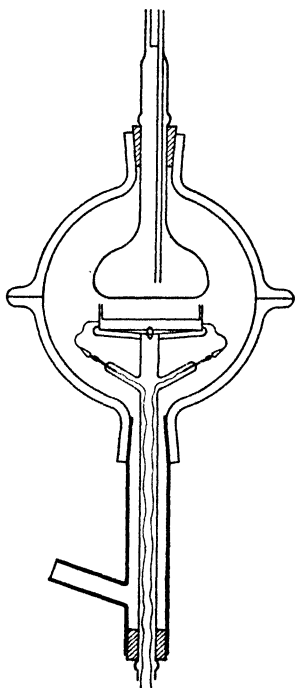


FIG. 64.—Molecular still constructed from two desiccator tops. (Carothers and Hill.)

All ground joints must be lubricated. A good grade of commercial-oil grease is satisfactory for most purposes. Burch⁵⁶ distilled ordinary petroleum jelly to 320° in a molecular still. The residue, consisting of 13 per cent of the original jelly, had a negligible vapor pressure at 10⁻³ microbars at 70°C. Such a grease can be employed free from any admixed material in vacuum work.

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CHAPTER VI

STEAM DISTILLATION

108. Steam distillation is another means of separating or purifying substances. Volatility is measured in terms of molecular weight and of vapor pressure in the presence of water. It may not bear any relationship to the vapor pressure of the pure compounds. Indeed, in many homologous series, such as the phenols, amines, alcohols, and aliphatic acids, the quantity that distills in steam is in exact reverse of what might be expected from the boiling points of members of the series. In other words the vapor pressures of the substances dissolved in water are markedly different from those of pure materials. These peculiarities make the method of steam distillation unique and especially important in organic chemistry. For convenience we may divide the types of compounds that distill in steam into two classes, those which are insoluble and those which are soluble in water. In the former class belong those substances, *e.g.*, hydrocarbons, whose vapor pressures are not substantially changed by the presence of water; in the latter class are such substances as acids, phenols, amines, whose vapor pressures are altered. This chapter will be devoted to a discussion of these two classes of compounds and to the rules that apply in predicting their behavior. The apparatus employed will be described. A section on steam distillation at reduced pressures is included. Other substances besides steam, such as mercury or petroleum fractions, may be employed in many instances. The use of these agents is discussed under the title of "Codistillation." Included in this chapter, also, is the subject of superheated steam.

109. Compounds Insoluble in Water.—Paraffin and aromatic hydrocarbons, alkyl and aryl halides, nitrobenzene, and other similar substances are not dissolved appreciably in water. Their vapor pressures, therefore, are those which the pure compound would have under like temperatures and pressures. The general

equation relating volatility to molecular weight and vapor pressure is

$$\frac{W_o}{W_w} = \frac{M_o P_o}{M_w P_w}$$

where W_o and W_w = the respective weights of organic compound and water in the distillate.

M_o and M_w = the respective molecular weights.

P_o and P_w = the corresponding vapor pressures.

As an example we may consider Naumann's¹ original application of this equation to naphthalene. At 98.2° and 733 mm. the amount of naphthalene that distilled with 49.4 g. of water was 8.9 g. From data in standard tables, the vapor pressure of pure water at this temperature is 712.4 mm. The remainder (733 - 712.4 = 20.6 mm.) is that of naphthalene. From the molecular weight of the two compounds (128 and 18) the amount of naphthalene that should have distilled over with this amount of water was 10.1, a value that agreed roughly with that actually obtained. In a similar manner Naumann showed that the equation was applicable to benzene, toluene, terpineol, carbon tetrachloride, nitrobenzene, ethyl bromide, and ethyl benzoate.

The higher members of a homologous series would have a reduced volatility in steam, as would be expected. Thus, from Naumann's data, 11.8 ml. of benzene, 4.7 mm. of toluene, and 2.3 ml. of xylene distill with every milliliter of water at 750 mm.

From theoretical considerations it is obvious that no true fractionation of compounds is possible by steam distillation. It has been shown, however, that in certain cases some degree of separation can be attained. Table 37 records data obtained by Lazarus² from the steam distillation of mixtures of 25 ml. each of two liquids. Fractions were cut as the temperature rose, and each portion then analyzed by dry distillation or other obvious method. With a mixture of aniline and nitrobenzene the temperature of distillation did not change sufficiently to be observed, but two cuts of 25 ml. each were made and analyzed. No suitable fractionation was possible in this instance, nor could benzene and toluene be separated.

110. Compounds Soluble in Water.—For a very large number of organic compounds that are soluble or partially soluble in water

the vapor pressures are appreciably altered by the presence of water. In this group it actually happens that substances of higher molecular weights and boiling points are more volatile in steam than the lower members of a homologous series. Sidgwick³ points out that the liquids are soluble to some extent in each other and therefore each has an effect on the vapor pressure

TABLE 37.—STEAM DISTILLATION OF MIXTURES OF COMPOUNDS

Mixtures of 25 ml. each of		Boiling point, °C.	Organic matter in distillate		
A	B		Total, ml.	A, ml.	B, ml.
Toluene.....	Nitrobenzene	90-95	21	19	
		95-98	6	3.5	
		98	23	23
Benzene.....	Nitrobenzene	96	23.5	22	
		96-98	4.	1.75	
		98	22.5	22.5
Toluene.....	Xylene	84-91	22	16.5	2
		91-98	28	3	18
Benzene.....	Carbon disulfide	64	22	19
		64-67	6	3
		67	22	21.5	
Terpineol.....	Nitrobenzene	95-97	21	19	
		97-98	4	2	
		98	25	2	24
Aniline.....	Nitrobenzene	98	25	15	10
		98	25	10	15

of the other. Hence distillation takes place at a higher temperature, and the proportion of substance in the distillate is altered. The general equation relating volatility to molecular weight and vapor pressure becomes merely a means of determining the vapor pressure of a substance in aqueous solution. But several methods have been utilized to give a quantitative expression of the amounts of water-soluble compounds distilled, and

efforts have been made to account for the greater volatility of the higher members of a homologous series.

111. The *Equation of Virtanen and Pulkki*⁴ states that

$$\frac{\log y_1 - \log y_2}{\log x_1 - \log x_2} = k$$

where x_1 and y_1 = the quantities of water in milliliters and of substance (parts per hundred) in the flask at the beginning of any period in the distillation.

x_2 and y_2 = the corresponding amounts at the end.

These investigators find that the value of k is a constant if the compound is pure and the conditions of distillation are standardized. By proper substitution in this equation the percentage distilled when 100 ml. out of an original 200 ml. is collected in the distillate (semidistillation value) or when 50 ml. (quarter-distillation value) is distilled or when 10 ml. is obtained can be calculated. Large values of k mean high volatility. In the following table are arranged the names of compounds, the values of k , and the semidistillation values. All results were obtained from distillation of the sample in 200 ml. of water from a 300-ml. Erlenmeyer flask. The values for k and for the semidistillation indicate clearly that higher members of a series are more volatile in steam than their homologues of lower molecular weight. Thus butyric acid is more than three times as volatile as formic acid; butylamine is twice as volatile as its lower homologue ethylamine; ethanol distills more rapidly than methanol. In the aromatic series the results are the same. The toluic acids are all more volatile than benzoic acids; methylaniline distills three times as fast as aniline.

When mixtures of compounds are distilled in steam, the values of k for individual substances are unchanged. This result makes it possible to use the method for *analysis of mixtures of acids*. As an illustration, a synthetic mixture of 47.4 ml. of 0.05 N acetic acid and 17.6 ml. of 0.05 N propionic acid was dissolved in 200 ml. of water. The total acidity found by titration with alkali was equivalent to 65 ml. of 0.05 N solution. Therefore, $A + P = 65$, where A represents the milliliters of acetic and P the quantity of propionic acid. After 100 ml. of water was distilled from the solution, the acidity of the distillate was found to be neutralized by 27.55 ml. of 0.05 N alkali. From Table 38, 36.6 per cent of the

TABLE 38.—VOLATILITY IN STEAM OF ORGANIC COMPOUNDS AS DETERMINED BY EQUATION OF VIRTANEN AND PULKKI

Compound	<i>k</i>	Semidistillation value
Formic acid.....	0.370	22.6
Acetic acid.....	0.657	36.6
Propionic acid.....	1.239	57.7
Butyric acid.....	1.96	74.4
Diethylacetic acid.....	4.57	95.4
Chloroacetic acid.....	0.047	3.2
Phenylacetic acid.....	0.070	4.8
Pyruvic acid.....	0.074	5.0
<i>o</i> -Toluic acid.....	0.508	29.7
<i>m</i> -Toluic acid.....	0.420	25.2
<i>p</i> -Toluic acid.....	0.378	23.1
Anisic acid.....	0.050	3.4
α -Crotonic acid.....	0.760	41.0
Benzoic acid.....	0.270	17.1
Salicylic acid.....	0.088	5.9
Cinnamic acid.....	0.102	7.4
<i>o</i> -Aminobenzoic acid.....	0.019	1.3
<i>m</i> - and <i>p</i> -Aminobenzoic acids.....	Not volatile	
<i>o</i> , <i>m</i> - and <i>p</i> -Nitrobenzoic acids.....	Not volatile	
Levulinic acid.....	} Distillable in too small quantities to obtain constants	
Glycolic acid.....		
Lactic acid.....		
Ammonia.....	13.0	
Methylamine.....	11.0	
Ethylamine.....	20.0	
Propylamine.....	30.0	
Butylamine.....	40.0	
Diethylamine.....	43.0	
Ethylenediamine.....	.02	1.4
Aniline.....	5.51	98.6
Methylaniline.....	16.0	
Benzylamine.....	3.27	89.6
α -Naphthylamine.....	1.05	51.7
Phenol.....	1.94	74.1
<i>p</i> -Chlorophenol.....	1.30	59.5
<i>p</i> -Nitrophenol.....	0.005	0.35
<i>m</i> -Nitrophenol.....	0.01	0.85
Thymol.....	12.0	
Formaldehyde.....	2.6	83.0
Acetaldehyde.....	Above 40.0	
Benzaldehyde.....	18.0	
Anisaldehyde.....	3.1	88.5
Methanol.....	8.9	
Ethanol.....	12.5	

acetic acid and 57.5 per cent of the propionic acid will have been distilled in that time. These quantities are related in the equation

$$0.366A + 0.577P = 27.55$$

By solving the simultaneous equations we obtain a value for acetic acid of 47.2 ml. and for propionic acid 17.8 ml., as compared with 47.4 and 17.6, respectively, in the original mixture.

Ternary mixtures of acids may also be analyzed. A solution, 200 ml., contained 23.6 ml. of 0.05 *N* acetic acid, 13.7 ml. of 0.05 *N* propionic acid, and 24.0 ml. of 0.05 *N* butyric acid. The total acidity was therefore equal to 61.3 ml. of 0.05 *N* alkali and was expressed by the equation

$$A + P + B = 61.3$$

where *A*, *P*, and *B*, refer to the foregoing acids in order. Two fractions of 50 ml. each were distilled. The values for the quarter distillation, obtained by suitable substitution in the equation of Virtanen and Pulkki, are 17.2 per cent for acetic, 30.0 per cent for propionic, and 43.0 per cent for butyric acid. For the first 50 ml. the acidity of the distillate was neutralized by 18.5 ml. of 0.05 *N* alkali. Therefore the equation for this portion of the distillation would be

$$0.172A + 0.300P + 0.430B = 18.5$$

The acidity of the second 50 ml. was neutralized by 15.7 ml. of standard alkali, making a total of 34.2 ml. for the first 100 ml. Using the values for the semidistillation of the respective acids, we have

$$0.366A + 0.577P + 0.740B = 34.2$$

Solving these three simultaneous equations, we find the quantities of acetic, propionic, and butyric acids to be equal to 23.2, 14.4, and 23.7 ml. of 0.05 *N* acid solution, respectively. These results are in error by -1.7 , $+5.1$, and -1.3 per cent. Similar calculations may be made for a mixture of four components, although the errors are greater. If the acids present in the mixture are not known in advance of the analysis, the determination is more complicated.

When using these values of k it is necessary that the conditions used by Virtanen and Pulkki be followed closely. The initial step is to obtain a solution of the acids to be analyzed free from carbon dioxide and salt. This is done by acidifying with sulfuric acid, refluxing for a short time, and then steam distilling until the last 200 ml. of the distillate has a constant small quantity of acid. In some cases this initial step can be facilitated by addition of salt, although if lactic acid is present in the mixture an error may be introduced, since this usually nonvolatile acid becomes distillable to a slight extent in the presence of salt. All of the distil-

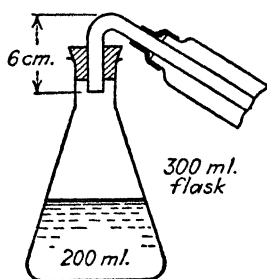


FIG. 65.—Apparatus used by Virtanen and Pulkki in determining constants of steam distillation.

lates are titrated with barium hydroxide. The solutions of barium salts are then united, concentrated in an evaporating dish, and transferred to a 250-ml. volumetric flask. The free organic acid is recovered by acidification with the exact amount of sulfuric acid, and the volume made up to 250 ml. After the barium sulfate has settled, 200 ml. of clear liquid is taken for analysis. It is put in an Erlenmeyer flask whose volume is precisely 300 ml. A wide tube connects flask to condenser, as shown in the illustration (Fig. 65). This close connection and relatively small flask help minimize condensation of steam on the walls so that values of k are very nearly constant. The flask is placed on a network of asbestos and heated by an ordinary Bunsen flame. During analysis the rate of distillation, which is very important, is adjusted so that 100 ml. will have distilled over in 60 min.

The percentage distilled is affected somewhat by the initial concentration of the compound in water. Thus, formic acid in 0.02, 0.24, and 0.53 per cent solution in water gave values of k equal to 0.364, 0.388, and 0.398, respectively. With butyric acid the value changed from 1.92 to 2.02 when the concentration varied from 0.05 to 2.29 per cent. Any difficulty arising from such a variation is usually not serious.

112. Although Virtanen and Pulkki have developed the general relationship for volatility of compounds soluble in water to a very high degree, they are by no means the only ones who

have presented data of this kind. The original observer was Duclaux⁵ who perceived that aliphatic acids were distilled in definite amounts in steam and proposed a system of analysis based on the quantities of acids present in the distillate. These numbers, now known as *Duclaux numbers*, represent the percentages of acids that distill over with each 10 ml. of water when the volume of the solution being distilled was originally 110 ml. Percentage may be based on the quantity of acid originally present in the 110 ml., as is done in Table 39, with data compiled

TABLE 39.—PERCENTAGE OF ACID, ORIGINALLY PRESENT IN 110 ML. OF SOLUTION, COLLECTED IN VARIOUS VOLUMES OF DISTILLATE

Volume of distillate, ml.	Formic	Acetic	Propionic	Butyric
10	4.2	6.4	11.2	16.4
20	8.5	13.0	22.2	31.2
30	13.2	19.7	32.7	44.8
40	18.2	26.7	42.9	56.6
50	23.4	34.1	52.7	67.3
60	29.3	41.6	62.0	76.2
70	36.0	49.9	70.9	84.0
80	43.6	58.7	79.1	90.1
90	53.0	68.5	86.7	94.8
100	65.3	79.9	93.6	97.8

by Gillespie and Walters;⁶ or may be based on the total amount of acid collected in the first 100 ml., as given in Table 40. Both Duclaux and Gillespie and Walters obtain more accurate results with the second method of calculation. Within the range of concentrations used, Duclaux numbers are not dependent on concentration or on the presence of other acids. There is some variation arising from differences in apparatus or manipulation which make it desirable for each investigator to prepare his own table of values. Usually 30 to 40 ml. of 0.1 *N* acid is made up to 110 ml. for each determination. The apparatus employed by Gillespie and Walters was a 200-ml. Erlenmeyer flask connected by a ground joint to a condenser. It was heated by an electric hot plate and kept warm around its upper part by a resistance-wire cage. One fraction was titrated while the next was collected. No special skill was required except in collection of

exactly 10 ml. The total time including that for titration of the 10 fractions was 50 min.

Where only one acid is involved, the application is simple, for the percentage in the first 10-, 20-, or 30-ml. portions should agree with that given in the table. For mixtures of acids an algebraic solution may be used. Gillespie and Walters describe a graphical method also.

TABLE 40.—PERCENTAGE OF ACID, COLLECTED IN 100 ML. OF DISTILLATE, THAT COMES OVER IN VARIOUS PORTIONS OF CONDENSATE

Volume of distillate, ml.	Formic	Acetic	Propionic	Butyric
10	6.5	8.0	12.0	16.7
20	13.0	16.3	23.7	31.9
30	20.2	24.6	34.9	45.7
40	27.8	33.5	45.8	57.9
50	35.9	42.7	56.3	68.8
60	44.8	52.1	66.2	77.9
70	55.2	62.4	75.7	85.8
80	66.8	73.4	84.5	92.1
90	81.2	85.7	92.6	96.8
100	100.0	100.0	100.0	100.0

113. *In Dyer's procedure* the volume of distilling liquid is kept constant at 150 ml. The organic acid is first titrated with 0.1 *N* alkali. Enough of the titrated acid solution is then added to the distillation flask to be equivalent approximately to 0.5 ml. of acid; the acid is liberated with 0.1 *N* sulfuric acid; and the volume increased to a total of 150 ml. The mixture is then steam distilled, a hot plate being used under the steam generator (a 2-l. flask) and another hot plate under the distilling flask (capacity 300 ml.). The second heater is used to heat the distilling mixture to the boiling point and to maintain constant-volume conditions. It is clamped loosely so that it can be swung out of position when not needed. Eight to ten pieces of stick zinc, each about an inch long, with a few drops of sulfuric acid are added to the steam generator to insure regular and smooth evolution of steam. Dyer's data for a number of acids are given in Table 41.

Dyer points out that when a single acid is steam distilled, the logarithm of the percentage of acid plotted against the milliliters

of distillate is a straight line. If a mixture of acids is present, the line curves, and the amount of curvature is dependent upon the distance apart of the two acids in a homologous series. By means of this relation the data in Table 41 can be corrected if desired for irregularities in the process. Analyses by the use of the numbers given in table are relatively simple. Each 10-ml. portion of distillate is titrated to find the acidity and the percentage of total acid calculated. If the logarithm of these percentage values

TABLE 41.—PERCENTAGE OF ACID STEAM DISTILLED WHEN VOLUME IS KEPT CONSTANT AT 150 ML.

Acid	Percentage of acid distilling over, ml.									
	10	20	30	40	50	60	70	80	90	100
Formic . . .	2.03	4.01	6.00	7.94	9.87	11.80	13.68	15.54	17.39	18.50
Acetic	3.56	7.08	10.50	13.74	16.91	19.90	22.78	22.54	28.15	30.66
Propionic . .	7.03	13.59	19.71	25.39	30.74	35.75	40.45	44.88	48.91	52.56
<i>n</i> -Butyric . .	11.47	21.68	30.54	38.78	45.80	51.92	57.22	61.93	66.14	69.88
Isobutyric . .	15.62	28.57	39.95	49.62	57.53	64.49	70.21	75.00	78.92	82.12
Isovaleric . .	19.03	34.10	46.48	56.43	64.74	71.39	76.97	81.28	84.64	87.51
Isocaproic . .	21.50	38.97	52.41	63.38	71.89	78.16	82.98	86.90	90.02	92.60
<i>n</i> -Caproic . .	22.59	39.07	51.28	61.29	68.86	74.84	79.73	83.52	86.94	89.75
Heptylic . . .	24.05	42.77	57.64	68.86	75.77	83.24	87.10	89.90	92.28	94.52
Caprylic . . .	33.85	53.57	65.68	75.77	88.19	91.30	93.48	95.03	96.58
Pelargonic	100.00

plotted against milliliters of distillate gives a straight line, the acidity of the solution is caused by the presence of only one acid. If these percentages should agree with any one of the columns of values given in the table, the identity of the acid would be revealed. If a mixture of two acids is present, and the identity of one is known, the other can be determined by the degree of deviation from a straight line in the graph suggested above. Algebraic analysis of mixtures is also possible.

114. *Stein*⁸ has expressed regularity in steam distillation of organic acids by means of the equation

$$-\frac{dx}{dv} = c(a - x)$$

TABLE 42.—CONSTANTS FOR STEAM DISTILLATION OF ORGANIC ACIDS
CALCULATED BY EQUATION OF STEIN

Acid	Total distillate, ml.	Acid in first 100 ml. distillate, %	Steam distilla- tion constant × 1,000
Formic.....	100.3	20.98	1.020
	100	22.02	1.063
Acetic.....	100	33.74*	1.74
	100.2	33.09	1.70
	101	12.46†	0.582
	100.7	45.28‡	2.59
Propionic.....	101.5	55.21	3.46
	101	58.51	3.62
<i>n</i> -Butyric.....	102	76.53*	5.65
	103.1	70.53	5.14
Isobutyric.....	100	79.3	6.26
	100.5	80.35	7.16
	103.0	80.85	6.68
Isovaleric.....	102	87.7	8.55
<i>n</i> -Capronic.....	103	91	10.13
	102	94	12.37
Hydroxyacetic acid.....	100	0.22	0.0085
Chloroacetic.....	100	3.43	0.152
Trichloroacetic.....	Decomposed		
Oxalic.....	100	0.01	
Malonic.....	100	0.30	0.0130
Benzoic.....	101.2	14.2	0.626
<i>o</i> -Toluic.....	101	26.17	1.47
<i>m</i> -Toluic.....	100.3	23.82	1.15
<i>p</i> -Toluic.....	102.7	18.09	0.991
	100.2	19.40	0.944
Phenylacetic.....	100.7	4.91	0.206
Salicylic.....	100	5.74	0.255
<i>p</i> -Hydroxybenzoic.....	100.1	0.01	
Mandelic.....	100.1	0.03	

* Volume in distilling flask maintained at 125 instead of 150 ml.

† Volume in distilling flask maintained at 500 ml.

‡ 15 ml. of concentrated sulfuric acid added to solution in distilling flask.

where a = the total amount of substance present in the original water solution.

dx = the amount distilled in volume element dv .

c = the constant of proportionality.

The quotient dv/dx is a measure of the distillation rate when volume rather than the customary time of distillation is taken into consideration. An integrated form of the equation is

$$-c = \frac{1}{v} \log \frac{a}{a-x}$$

The value of this constant, multiplied by 1,000 and considered in the reverse sense in order to make it positive, is shown for a number of acids in Table 42. Constant-volume conditions were employed during each determination, although the original volume was not the same in each experiment. Some of the fluctuations in the value of the constant c may be attributed to this condition.

115. As an *explanation for reduced volatility* of water-soluble compounds, Virtanen and Pulkki suggest the property that water has of hydrating substances that it dissolves. From this standpoint, compounds with polar groups which might be hydrated are less volatile than others. Thus, benzoic acid is not so volatile as benzene, nor is butyric acid so volatile as butane, because the acids have the polar carboxyl groups in their molecules. As the percentage of carboxyl per molecule decreases upon ascending a homologous series, the compounds become progressively more volatile. For example, the toluic acids are distilled more rapidly than benzoic, caproic more rapidly than butyric. In other words the anchor that serves to hold formic or acetic acid in solution is not so effective in holding down the higher members of the series where the proportion of hydrocarbon per molecule is increasing. The same considerations can be applied to other series such as alcohols and amines. When the number of polar groups in a molecule is increased, volatility falls off. Chloroacetic acid is less volatile than acetic; anisic, less than benzoic. Levulinic, glycolic, and lactic acids are distillable in small quantities only.

Data that might suggest some parallelism between values of h and free energy of hydration are not entirely lacking. Butler and

Ramchandani⁹ have determined this value for a number of compounds by means of the relation

$$RT \log p/N$$

where p equals the partial pressure of solute over a very dilute aqueous solution of molar fraction N . Whether the suggested relationship is real or coincidental the values recorded in Table 43 show that the free energy of hydration and the steam-distillation constant change in a similar direction. The table further suggests that nitriles and esters would be far more volatile in steam than the corresponding acids or amines. In other words, conversion of an acid to its ester might prove a suitable means of rendering it volatile in steam in cases where purification by other methods was difficult.

Although the proposed relation of nonvolatility to hydration appears novel and interesting, reference should also be made to an opinion of Reilly and Hickinbottom¹⁰ that the electrolytic dissociation constants of volatile acids might have an important bearing on the subject. An earlier suggestion that the degree of association of the acids had a considerable effect on volatility was made by Richmond.¹¹ Moreover, mutual solubility of the two liquids in each other is of fundamental importance.

TABLE 43.—FREE ENERGY OF HYDRATION OF VARIOUS ORGANIC COMPOUNDS THAT DISTILL IN STEAM

Compound	p	$RT \log p/N$	Virtanen and Pulkki's steam-distillation constant k
Acetic acid.....	1500	0.657
Propionic acid.....	0.093	1730	1.239
Butyric acid.....	0.047	1850	1.96
Ethylamine.....	0.204	3580	20
<i>n</i> -Propylamine.....	0.236	3720	30
<i>n</i> -Butylamine.....	0.378	3830	40
<i>n</i> -Propionitrile.....	1.75	4360	
<i>n</i> -Butyronitrile.....	2.15	4560	
Acetone.....	4800	
Methyl acetate.....	1.92	4890	
Ethyl acetate.....	5.44	5110	

116. The Effect of Salt.—When salt is added, a very great change in the value of Virtanen and Pulkki's constant is found. All salts do not behave alike in this respect. Sodium chloride is much more effective in raising the value of k than is calcium

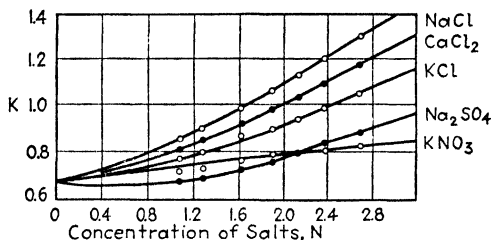


FIG. 66.—Effect of salts at varying concentrations on steam distillation of acetic acid.

chloride, potassium chloride, sodium sulfate, or potassium nitrate (see Fig. 66). Indeed, the constant is actually a little lower with small quantities of sodium sulfate. Sodium chloride was also found to be more effective than the nitrate or sulfate salts in promoting steam distillation of benzoic acid. Neither is the change in the value of k the same for all acids when distilled from

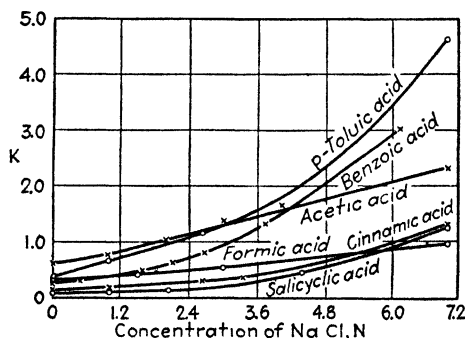


FIG. 67.—Effect of varying concentration of salt on steam distillation of different organic acids.

solutions having equal amounts of sodium chloride. Thus we observe in Fig. 67 that only slight changes occur in the cases of formic and salicylic acids as contrasted with very considerable increases for benzoic and toluic acids. This effect of salt cannot be attributed to mere elevation of boiling point, because equal

mol concentrations of different salts do not produce the same result. Furthermore, glycerol and sodium acetate were added in amounts sufficient to produce a boiling-point elevation equal to that caused by the presence of sodium chloride without effecting any increase in the value of the constant k . This fact influenced Virtanen and Pulkki in their opinion that salts possessed a specific

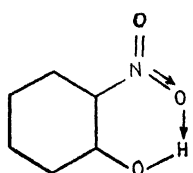


FIG. 68.—Chelate-ring structure of *o*-nitrophenol.

influence such as an alteration in the hydration of the organic acid. Their belief is in agreement with the fact that sodium chloride has a greater effect in reducing solubility of the organic acid in water than have the other salts in question and that adsorption of fatty acids¹² on carbon from aqueous solutions is made more effective by use of common salt.

117. Volatility of Ortho-substituted Compounds.—Volatility in steam of some ortho-substituted compounds is of considerable importance in separating them from their meta and para isomers. This phenomenon receives a ready explanation if we consider the ability of polar molecules to associate, either with themselves or with water, and the property of some ortho-substituted molecules

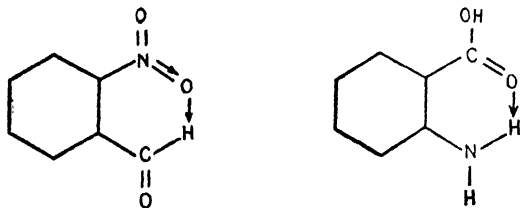


FIG. 69.—Chelate rings in *o*-nitrobenzaldehyde and *o*-aminobenzoic acid.

in forming chelate rings. The formula of ortho nitrophenol, for example, may be written as having a chelate¹³-ring structure (Fig. 68) in which the hydrogen atom of the hydroxyl group is bound by a coordinate or singlet valence to the oxygen atom of the nitro group. Since this structure pictures the residual affinity of the polar group as internally saturated by an adjacent group, there is less likelihood that this molecule would be associated with others. It would also be less soluble in water and more volatile in steam. In contrast to the behavior of ortho-substituted compounds, the meta and para isomers have no adjacent groups by which their residual affinity may be satisfied internally. They

associate with each other or with water, thus rendering them less volatile in steam. Chelate-ring formation would be possible also in *o*-nitrobenzaldehyde and *o*-aminobenzoic acid (Fig. 69), both of which are volatile in steam in contrast to the behavior of the meta and para compounds (see Table 38). In further agreement with this view is the nonvolatility of ortho-chlorobenzoic acid, for which no five- or six-membered chelate-ring structure is possible.

Sidgwick and Dash¹⁴ have tested the volatility of a number of *o*-, *m*-, and *p*-isomers and shown that abnormal values occur where chelation is possible. In the table below, the volatilities

TABLE 44.—RELATIVE VAPOR PRESSURES IN STEAM, REFERRED TO THE PARA ISOMER

Disubstituted benzene compound	Ortho	Meta	Para
CH ₃ , CH ₃	0.79	0.86	1
CH ₃ , NH ₂	1.04	0.87	1
CH ₃ , Cl	1.10	0.90	1
CH ₃ , NO ₂	1.65	1
CH ₃ , OH	1.72	1.03	1
NH ₂ , Cl	2.47	1.10	1
COOH, Cl	4.01	4.38	1
CH ₃ , COOH	4.49	2.81	1
NHCOCH ₃ , Cl	6.61	0.60	1
COOH, NO ₂	20.9	7.3	1
NHCOCH ₃ , NO ₂	43.1	2.00	1
NH ₂ , NO ₂	47.9	9.49	1
OH, NO ₂	160.	3.32	1
OH, COOH	1320.	5.0	1

of *o*-nitro- and *o*-chlorobenzaldehydes are only slightly abnormal, while those of *o*-nitroaniline and *o*-nitrophenol are very abnormal. Great abnormality is also shown by pyrocatechol, *o*-hydroxybenzoic acid, *o*-hydroxybenzaldehyde, *o*-nitrophenol, or *o*-chlorophenol. Distinct abnormality is found in *o*-nitroaniline, *o*-nitrobenzoic acid, *o*-aldehydobenzoic acid, anthranilic acid, or *o*-phenylenediamine; nearly normal volatility is observed with *o*-chloroaniline, *o*-chlorobenzoic acid, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, *o*-chloronitrobenzene, or *o*-dinitrobenzene.

According to Sidgwick an ortho compound, to have abnormal volatility, must contain (1) a group which makes it sensitive and (2) a group which can act upon this sensitiveness.

Comparison of results with mono-, di-, and trinitrophenols¹⁵ is exceedingly interesting, since they show that chelation is confined to a single group. Introduction of a second nitro group, even in the other ortho position, does not cause a further increase in volatility. Actually, the volatility is reduced (see Table 45). This result is indeed as expected if the effect of the nitro group in the ortho position is a structural one, for only one nitro group is needed to effect formation of a chelate ring. Nearly all of the dinitrophenols in which one nitro is adjacent to the hydroxyl

TABLE 45.—RELATIVE VAPOR PRESSURES IN STEAM OF NITRO-SUBSTITUTED PHENOLS

Substance	Vapor pressure of the phenol, mm. \times 100	Solubility, 100°C.	Relative vapor pressures
Nitrophenol, <i>o</i>	283.0	1.08	160
<i>m</i>	5.87	47.7	3.32
<i>p</i>	1.77	42.3	1
Dinitrophenol, 1,2,3-.....	5.48	7.8	3.10
1,2,4-.....	22.8	1.5	12.9
1,2,5-.....	44.8	1.4	25.3
1,2,6-.....	11.0	1.3	6.20
1,3,4-.....	0.103	15.0	0.0582
Picric acid.....	0.249	6.33	0.441

group have a volatility greater than that of *m*- or *p*-nitrophenol. When the nitro group is further removed, as in the 1,3,4- compound, the volatility falls off sharply. The relationship is made clear also by reference to nitrobenzene which is less volatile than benzene. In a similar manner any nitrochelated ring compound, *e.g.*, 1,2,4-dinitrophenol, would be less volatile than the unsubstituted chelate substance *o*-nitrophenol, and the dinitro chelated ring compound, *e.g.*, picric acid, would be even less volatile.

Solubility in water of the nitro-substituted phenols is also given in Table 45. In general, chelated-ring compounds are

soluble in water and more soluble in organic solvents than their isomeric *m*- and *p*- compounds. While it is true that the four least soluble compounds are also the most volatile, an exact relationship between volatility and insolubility is not possible, as witnessed by the fact that *m*-nitrophenol is both more soluble and more volatile than its *p*-isomer. The broad generalization is, however, helpful in predicting possible volatility of isomeric compounds.

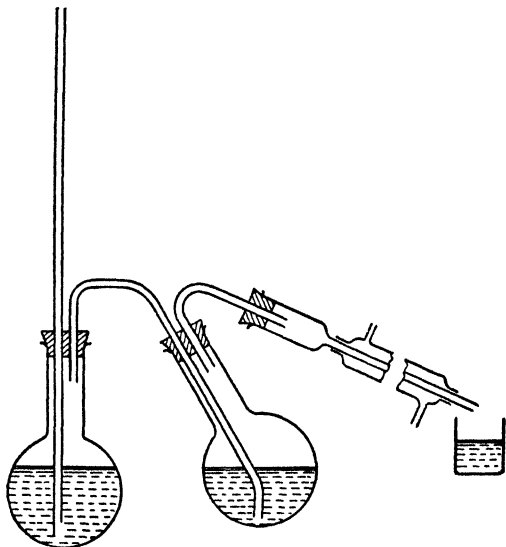


Fig. 70.—Conventional apparatus for steam distillation.

Neither is greater volatility of any one compound as compared with its isomers solely or necessarily related to the chance that chelation may occur. Thus the isomeric 1,2,*X*-dinitrophenols vary in their volatility according to the position of the second or *X* nitro group. Mention might also be made of the separation by steam distillation of the volatile 2-amino-6-chloropyrimidine¹⁸ from its nonvolatile isomer 2-chloro-6-aminopyrimidine, although no chelation is possible in either case.

118. Apparatus and Procedure.—Conventional apparatus for steam distillation, shown in Fig. 70, comprises a steam generator, distilling flask, condenser, and receiver. Many variations of this

form may be employed. It is not necessary, of course, to use a separate steam generator. Water (or salt solution) may be added to a distilling flask, and heat applied directly. In such a simplified apparatus the problem of bumping may become acute. Suggestions have already been given to help in avoiding this difficulty in ordinary distillations (see Sec. 92). An apparatus for micro steam distillation has been suggested by Pozzi-Escot¹⁷ which consists (Fig. 71) of a specially constructed test tube inserted in the neck of a distilling flask. It follows from the discussion of Sec. 116 that use of a saturated salt solution when steam distilling will shorten greatly the time required for distillation as well as render many compounds volatile that are steam distilled with difficulty. Frequently it is advantageous to defer addition of salt until the more volatile compounds have been removed.

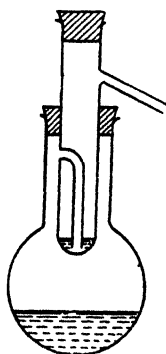


FIG. 71.—Pozzi-Escot's apparatus for steam distillation on a micro scale.

119. Steam Distillation at Reduced Pressures.

Steam distillation may be carried out at pressures below atmospheric. The same considerations relating volatility to vapor pressures or solubility should apply. Temperature of volatilization is, of course, considerably lower. Steinkopf¹⁸ observed that aniline distilled in steam at 23°C./20 mm. and nitrobenzene came over at 22.5°C./19 mm. Toluene distilled at 27°C./27 mm., but a separation of toluene from nitrobenzene as carried out by Lazarus at atmospheric pressure was not possible under these conditions. He also applied reduced pressure in distilling compounds normally decomposed by water. Benzoyl chloride was found to be volatile in steam at 21°/16 to 17 mm. and was recovered unchanged in the distillate to the extent of 40 per cent. The greatest use of steam distillation at reduced pressures lies in the recovery of very high-boiling substances. Offermann¹⁹ distilled fats, resins, and tars with steam under a vacuum. In many cases where such distillations are performed the temperature of the distilling flask must be increased to a point where an aqueous phase is no longer present. Such cases will be discussed in more detail under the use of superheated steam (Sec. 121).

120. Codistillation.—Codistillation (*Kondestillation*) is a term applied by Rassow and Schultzky²⁰ to the distillation of any compound simultaneously with another substance. According to them, steam distillation is only a special phase of a general subject. Other agents might be substituted frequently with advantage. Four conditions are suggested for consideration in choice of an agent:

1. The agent must dissolve the distillable substance with difficulty or not at all.
2. Its vapor pressure must be near that of the other compound.
3. Its molecular weight must at least not be greater than that of the distillable compound.
4. It must be as cheap as possible.

Water fulfills these conditions in a large number of cases. It fails, however, to function as an agent for a compound such as *p*-nitrophenol, whereas a high-boiling petroleum fraction serves most admirably and gives a product that is purer than that obtained by ordinary methods. The products of nitrating phenol in acetic acid are first subjected to steam distillation to remove the ortho isomer. The residue is then dried by distilling with benzene. It is next freed from acetic acid by distilling with a relatively low-boiling petroleum fraction (b.p. 220 to 260°/760 mm.). Finally, the residue is subjected to codistillation with a higher petroleum fraction (b.p. 130 to 160°/16 mm.). The *p*-nitrophenol in the distillate, being insoluble in the petroleum, is easily separated from the latter. The yield is 85 as compared with 50 per cent by the ordinary method of separation by crystallization. The product is also free from tars.

Indigo may be distilled without decomposition with high-boiling (190°C. and up) kerosene. The product is insoluble in the distillate and is recovered in very pure condition. For higher temperatures Nujol or mixtures of Nujol and kerosene may be used. Crude dibenzanthracene can be distilled under such conditions with considerable improvement both in melting point and in physical appearance of the crystals. With such high-boiling solvents the product crystallizes rather slowly, so that it may be necessary for the distillate to stand overnight to obtain material in a form suitable for filtration. The oil adhering

to the crystals is washed off or removed by digestion with petroleum ether.

Mercury²¹ has been recommended as an agent for codistillation with high-boiling materials. Many aromatic hydrocarbons such as chrysene, pyrene, fluoranthene, and anthracene are distillable with this metal. As would be expected, the mixture distills below the boiling point of pure mercury. The method is recommended also for the distillation of phenylquinoline and indigo, although in the latter instance some decomposition is apt to occur.

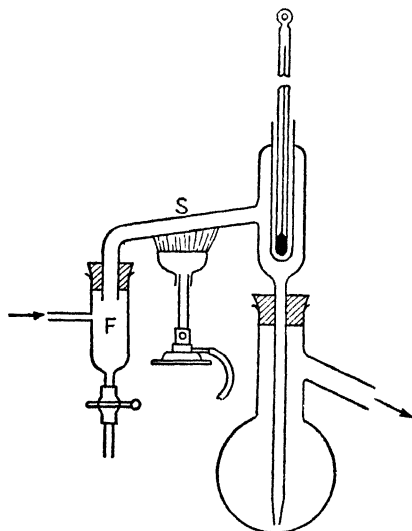


FIG. 72.—Superheated-steam-distillation apparatus.

Use of mercury often has the general disadvantage of producing a fine colloidal dispersion of the metal through the solid distillate which is inconvenient to remove. Moreover, there is constant danger from poisoning. In general, more satisfactory results can be secured by use of a petroleum fraction of high boiling point or by application of superheated steam.

121. Superheated steam is in many respects an ideal agent for recovery of high-boiling compounds. The components separate cleanly in the distillate, and expense is trifling. To secure the greatest satisfaction it is necessary to have good control of the temperature of superheating. The apparatus shown in Fig. 72

has been in use in the author's laboratory for some time and has been found to give a satisfactory and reproducible performance. It has an advantage in that the superheater *S* is placed so close to the inlet that a minimum cooling of steam results before it enters the flask. Construction is very simple. A section of glass tubing (10 mm. outside diameter or larger) is wrapped with a few layers of wire gauze and heated with a wing-top burner. The gauze should be supported by a clamp to prevent the tubing from sagging at high temperatures. A thermometer is placed in the vapor path just before the inlet. To prevent cracking of the thermometer bulb it is convenient to insert it in a glass (pyrex) well. Slugs of water from the steam generator or line are trapped in the funnel *F*, and the superheater tube is inclined slightly toward this funnel so that any condensed liquid may drain. The flask is heated in an oil bath. The usual practice is to keep bath and vapor temperatures the same. Conditions of distillation can thus be recorded and reproduced at will. In recovering products of nitration of aromatic systems, the ortho derivative can be removed by ordinary steam distillation. The temperature can then be raised, and the para compound distilled. When the product of nitration of *p*-methylbiphenyl was distilled, the low-boiling isomer was recovered by maintaining the temperatures in the vicinity of 150°C., and the high-melting isomer obtained in nearly pure condition (m.p. only 2° low) at 200°. A tarry mass from an uncontrolled Friedel and Craft reaction was subjected to the action of superheated steam at 200°, and a mixture of crystalline material recovered very easily. The mixture of trinaphthalenebenzene and dinaphthalenethiophene resulting from Rehländer's²² fusion of acenaphthene with sulfur can be separated more readily with superheated steam (temperature as high as 325°) than by crystallization. The upper limit of temperature with such an apparatus is a matter of the stability of the compound and the inconvenience arising from softening of the glass. In the apparatus used in this laboratory the pyrex tubing in the superheater has been replaced by a quartz section to avoid this difficulty. If ground joints are used in such an apparatus, they should be loosened immediately after distillation has been completed.

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CHAPTER VII

CRYSTALLIZATION

122. The problem of crystallization is nothing more than that of effecting an arrangement of molecules that permits them to deposit from a supersaturated solution in well-defined aggregates. The process is one of the most important steps in the laboratory, yet the laws that underlie the operations are not always understood by the average manipulator. For successful work the danger of cooling too much, the need of occasional warming, the specific effect of scratching, and many other phenomena related to the process should be realized. Not only is emphasis placed on an understanding of these physical factors, but attention is directed to the importance of prior methods of purification. Indeed, it can be stated as a general rule that crystallization of a very crude product should never be undertaken until other methods of purification have been applied. The reasons for this generalization will appear obvious after reading the section on effect of purity. How and when to crystallize, with many illustrations of difficulties overcome, forms a considerable part of the discussion in this chapter.

123. Effect of Purity of Compound.—Presence of impurities frequently impedes the rate and completeness of crystal formation. Mashimo and Shishido¹ found that the yield of glutamic acid hydrochloride from soybean oil was diminished greatly by impurities. In crystallizing petroleum wax,² high-boiling colloids were found to act as inhibitors. Velocity of crystallization of *d*-dimethyltartrate³ diminished greatly when impurities were present. Even the very similar optical isomer and a racemate acted as retardants. In crystallizing rubber,⁴ the need of purity, particularly freedom from nitrogenous compounds which might be adsorbed on the crystal nuclei, is emphasized. An oily product, resulting from the cleavage of a β -oxanol by ethylmagnesium bromide,⁵ failed to crystallize until it had been steam distilled. The distillate yielded the solid crystalline compound

diphenylethylcarbinol. Since water is an impurity, it is sometimes necessary to dry the solvent thoroughly before crystals will form. Sucrose⁶ of 72 per cent purity has been shown to crystallize twice as fast as a 70 per cent pure sample but only one-fifteenth as fast as pure sugar. Although a material will crystallize more readily the purer it is, there is no assurance that ready formation of crystals or large size of crystals is a criterion of purity. Acenaphthene,⁷ distilled and then crystallized from 95 per cent alcohol, formed crystals 3 to 5 cm. long yet melted several degrees too low. An explanation for the effect of impurities in slowing down the rate is that such agents form stable adsorption complexes⁸ which retard orientation of dissolved substances on the crystal surface.

124. The importance of *purity prior to attempts to crystallize* cannot be stressed too much. Too often the product of a reaction is subjected to crystallization with resulting loss of material. It should be remembered that removal of impurities in this manner usually results in lower yield of the desired product. Loss occurs not only from the inevitable solution of product with impurities but also from a retardation in rate of crystallization, sometimes to the practical failure of any crystals to form. References have already been made to the gain in yield when a product was first distilled in vacuum (see Sec. 89) or codistilled with a petroleum fraction (Sec. 120). These instances are typical of what can be accomplished when an initial crystallization is replaced by other methods. Steam distillation, with and without the presence of salt; vacuum distillation; exhaustive digestion (Sec. 59) with a poor solvent; extraction in a Soxhlet apparatus; thorough drying or removing of solvent such as can be accomplished only with a mercury-condensation pump are of the greatest service in producing a product that will crystallize rapidly in good yield. The first step, therefore, in any crystallization process is to have the material as pure as possible.

125. Choice of a Solvent.—The solvent for use in crystallization can be determined only by experiment. The usual method is to put small quantities (5 to 20 mg.) in test tubes, add 0.5 to 1.0 ml. of each solvent, warm to effect solution, and observe which produces the best and largest quantity of crystals. As a general rule, that solvent will be preferred in which the com-

pound is soluble when hot but insoluble when cold. The paraffin hydrocarbons petroleum ether or ligroin are usually tried first, because the solubilities of a large number of organic compounds in these solvents at room temperature are ordinarily very slight. For the same reason these solvents are favored as diluents for organic liquids that dissolve compounds too easily. Their mixtures with ether or benzene, for example, frequently make ideal combinations for obtention of crystals. For a similar reason mixed solvents composed of water with methanol, ethanol, and acetone are useful. Methanol itself is an excellent diluent for other organic solvents. The influence of heat is very marked in solutions. At higher temperatures, as represented by the boiling points of nitrobenzene, chlorobenzene, tetralin, etc., many of the individual differences that make one solvent so markedly better than another at room temperature become insignificant. Kerosene, preferably purified by distillation, is, in fact, often as good a solvent when hot as is nitrobenzene. Its main disadvantage is that it is such a poor solvent when cold that it holds back very little of some impurities in the mother liquor. It can, however, be used successfully as a diluent for higher boiling solvents.

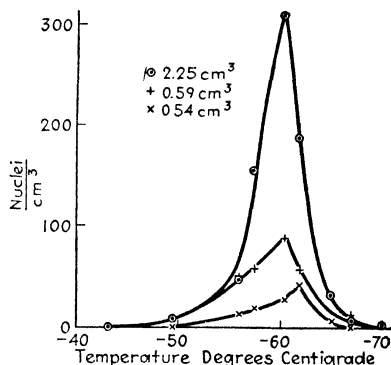


FIG. 73.—Effect of temperature on formation of crystal nuclei of glycerol.

126. The Effect of Cooling.—Freezing at extremely low temperatures will not always produce crystals. Indeed, it is possible to cool so much that crystallization does not occur. The melting point of a sample of glycerol (the middle fraction of a double distillation boiling at 165 to 170°/9 mm.) was 19.5°. Tammann and Jenckel⁹ studied the rate of formation of crystal nuclei of this compound and found a maximum between -60 and -62°. The curve picturing their results is reproduced in Fig. 73. It shows that in a given time (20 min.) few if any crystals form at -50°; a maximum number occur at -60 to -62°; and no crystals form at -70°. Some variation occurred

in the number of crystal nuclei formed with different amounts of glycerol, but the optimum temperature remained approximately the same. This variation can be ascribed to different amounts of water adsorbed in manipulation. Formation of crystal nuclei under conditions employed by these investigators is clearly within a narrow temperature range.

Once crystals have formed, it might be supposed that they would grow in size rapidly under the same conditions. The contrary is the case. The maximum velocity, as judged by a dilatometer method, for crystal growth of glycerol is reached

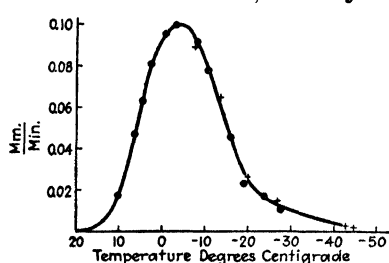


FIG. 74.—Effect of temperature on growth of crystals of glycerol.

when the temperature is -3.5° (Fig. 74). At -20° the rate of growth is not more than 20 per cent of that at the maximum, and at -45° it is practically zero. The ideal temperature for inception of crystallization is thus seen to be far different in this case from that for rapid increase in crystal size.

Optimum temperature conditions exist for other compounds¹⁰ as well. Table 46 lists temperatures at which a maximum

TABLE 46.—OPTIMUM TEMPERATURES FOR FORMATION OF CRYSTAL NUCLEI IN VARIOUS COMPOUNDS

Compound	Temperature for maximum number of nuclei, °C.	Melting point, °C.	Difference, °C.
Piperine.....	40	127	87
Betol.....	16	95	79
Santonin.....	40–50	170–120	130
Narcotine.....	140	175	35
Allylthiourea.....	–20–0	74–70	94
Chlorourethan.....	20	102	82
Quinic acid.....	50	161	111

number of crystal nuclei of a number of compounds are formed. These values average 88° below the melting points.

The foregoing results should be kept in mind when crystallizing compounds, particularly from sirupy or tarry media. Cooling to low temperatures such as can be reached with solid carbon dioxide may render the mass so viscous that no crystals will form. After any such cooling the medium should be allowed to warm slowly in the hope that it will pass through an optimum region for formation of minute crystals. Once crystals have been observed, it is very probable that their size will be increased by keeping the mixture at a higher temperature.

In the case of large samples of material it is sometimes advantageous after cooling to heat gently one side of the beaker by a current of warm air in order to establish a heat gradient through the medium which will enable an optimum temperature to be attained in some part of the mass. Another useful method is to add a few lumps of solid carbon dioxide in order to produce a number of cold spots here and there in the material being crystallized. This method is particularly advantageous with viscous sirups. It must always be remembered that crystallization is a time factor. Extreme patience is necessary. If all methods fail to induce crystal formation within a reasonable time, the mixture should be set in an ice chest and allowed to stand for over a year before conceding failure. Such a long period of time will insure that the operator has given the mass a reasonable opportunity even if the temperature is not ideal.

127. The Effect of Surface.—Schaum and Riffert¹¹ studied formation of crystal nuclei under a microscope and observed that the number was more numerous toward the outer edges. On repeated meltings nuclei appeared several times at the same spot. This so-called "memory" in crystallization has been ascribed by some investigators to loose aggregates present in the melt and by others to colloidal dust particles on the glass. Unless unusual conditions are employed, crystals grow from a surface, either solid or liquid, into the solution rather than from the interior outward. This fact results from orientation of molecules upon solid surfaces or interfaces. Advantage may be taken of this tendency when working with compounds that crystallize with difficulty. Size and shape of the container should be such as to give a maximum exposure of surface. Thus, we often obtain small quantities of crystals for seeding purposes by cooling

a very thin film of liquid to low temperatures. One or two drops of material put into a test tube or beaker and spread into a thin film by rotating the container can frequently be made to crystallize by cooling in a freezing mixture where a large quantity would act sluggishly. A cover glass or the bottom of a beaker may also be used in place of the test tube. Spreading of a viscous material over such a surface is often facilitated with a few drops of a solvent. A very useful method¹² is to wet a glass bead with the substance, put it into a test tube, and cool in carbon dioxide snow to produce crystals on the surface of the bead. It can then be rolled out of the tube into the larger quantity of material, previously cooled to a temperature below the melting point of the compound. When done in this manner, there is no need for scraping the surface to obtain seed crystals, a process sometimes accompanied by fusion of impure or low-melting compounds. Some variation of the rate of warming or cooling may be had by changes in the size or shape of containers.

TABLE 47.—PARTIAL DEACTIVATION TEMPERATURES FOR VARIOUS ADSORBENTS WITH SALOL AND BENZOPHENONE

Adsorbent	Salol, °C.	Benzophenone, °C.
Mercury.....	10	10
Ignited ferric oxide.....	10	10
Brass filings.....	10	10
Pulverized mica.....	80	50
Ground pyrex.....	80	70
Roll sulfur.....	60	50
Silica gel.....	80	70
Powdered quartz.....	110	140
Active carbon.....	150	110

The effect of dust particles in causing crystals to appear repeatedly at one spot after melting and cooling has been mentioned at the first of this section. Richards¹³ has shown that this phenomenon varies with the material on which crystals form. Thus when salol crystallizes in the presence of brass filings, the sample need be heated only 10° above its melting point in order to destroy all tendency to crystallize spontaneously on the brass when cooled. On mica, however, the solid retains its ability to

seed salol until it has been heated 80° above its melting point. The phenomenon is attributed to a preservation of the crystal form on the solid surface even above the melting point of the compound in question. The deactivation temperature, *i.e.*, the temperature to which a mixture of compound and adsorbent must be heated to destroy, in part at least, all "memory" of crystallization, varies widely with different compounds and may be as high as 150° above the melting point. Some data are given in Table 47.

128. Influence of Fluidity.—Addition of a solvent is helpful when the solution is viscous. Frenkel¹⁴ has found that linear velocity of crystallization is inversely proportional to viscosity of solution. This fact would be expected from the necessity for proper orientation of the molecule. In the crystallization of rubber, referred to later, the fluidity was made high enough to provide sufficient mobility for formation of nuclei. Dilution below that point reduced the number of nuclei to a minimum.

A relation of viscosity to velocity of crystallization has been shown by Jenkins¹⁵ in a study of the effect of a number of solvents

TABLE 48.—EFFECTS OF SOLVENTS ON VELOCITY OF CRYSTALLIZATION OF UREA

Solvent	Percentage by volume	$K \times 10^4$	Specific viscosity of solution
Methyl alcohol } Ethyl ether }	50	392	0.41
Methyl alcohol	256–272	0.76
Ethyl alcohol	158–183	1.47
Ethyl alcohol } Glycerol }	76 24	55	9.90
Methyl alcohol } Glycerol }	50 50	32–36	37.3
EFFECT ON CRYSTALLIZATION OF ACETANILIDE			
Ethyl acetate	450–460	0.390
Methyl alcohol	212–273	0.701
Amyl alcohol	75–85	5.9
Glycerol } Methyl alcohol }	50 50	16	56.0

on crystallization of urea and acetanilide. The equation used in calculating is given in Sec. 133. The data (Table 48) indicate that high viscosity is accompanied by low rate of crystallization. For the case of pure solvents this relationship can, indeed, be expressed by an equation relating viscosity η to velocity K of crystallization.

$$K = \frac{\text{constant}}{\eta^{0.59}}$$

This mathematical expression fails when collodion is added, showing that the latter has a specific effect.

129. Seeding.—Seeding is especially helpful, since it provides crystal nuclei of a definite and desired pattern. Contrary to observations of Ostwald that particles containing about 10^{18} or 10^{12} molecules no longer have inoculating power, Tammann and v. Gronow¹⁶ found that aggregates containing 10^7 times as many atoms were successful in inducing crystallization.

Seeding may be done not only with crystals of the compound desired but also with true isomorphs. Where a solution is supersaturated with respect to more than one substance, seeding will promote crystallization of the like compound but not of others. Dufraisse¹⁷ found that the usual methods of separating cis-trans isomers of diiodobenzalacetophenone were useless but that either could be isolated from a slightly supersaturated solution of the mixture by addition of a few seed crystals of the desired isomer. This method is of greatest utility where it is possible to obtain the necessary small quantities of seed crystals by exhaustive digestion, distillation, or other method.

130. Scratching and Rubbing.—Scratching the side of a beaker often initiates crystallization. The effect may be ascribed to breaking off of small particles of glass or to roughening the surface. The crystals are thus oriented more rapidly than on smooth glass. Rubbing is similar in its general results, although no minute particles of glass are broken off. It is usually done with a small quantity of an organic liquid in which the compound is slightly, if at all, soluble. The viscous mass, covered with a little liquid, is rubbed with a stirring rod or ground in a mortar until crystals have formed. It may be necessary to work the mass for an hour before inducing solidification.

131. Radium Emanations: Electric and Magnetic Fields.—

Since a problem in crystallization is that of proper orientation of molecules, it would be expected that an electric or magnetic field and radium emanations would exert considerable influence on molecules having a polar group. Such is indeed the case. Salol and piperine, placed on cover glasses under a microscope and exposed to an electric field in parallel and to a magnetic field at right angles to the glass, exhibited a marked increase in the number of crystal centers formed. In Table 49 data for

TABLE 49.—RATE OF CRYSTAL FORMATION WHEN EXPOSED TO RADIUM EMANATIONS OR ELECTRIC FIELD

Time from beginning of observation on salol, hours.....	22	70	92
Number of crystal centers under radium.....	10	20	28
Number under the electric field.....	85	206	254
Number with no outside influence.....	0	1	2

crystallization of salol under various external stimuli are recorded. The films of liquid were 0.05 to 0.06 mm. thick, and the electric field was obtained from electrodes 0.4 mm. apart under a potential of 450 volts. The radium emanation was from 5 mg. of bromide salt. The influence of a magnetic field of 9,000 to 10,000 gauss on the formation of crystal nuclei on the same compound is shown in Table 50. Kondoguri¹³ concludes from these experiments

TABLE 50.—FORMATION OF CRYSTALS UNDER MAGNETIC FIELD

	Salol	Salol	Piperine
Temperature, °C.....	17–27.5	14–22.7	17–29.2
Time from beginning, minutes.....	200	180	175
Number under magnetic field.....	127	15	27
Number with no field.....	3	1	7

that for equal time intervals the number of crystal centers forming is approximately proportional to the electric or magnetic field strength. With constant field the number of crystal nuclei increases with time up to a limiting value.

An electric field has also been applied by inserting glass rods, holding electrodes, into a beaker containing the compound to be crystallized. The relationship between strength of electric

field and time of crystallization of nitrobenzene (m.p. 5.7°) under such conditions can be judged from the data in Table 51. In connection with this work an interesting observation by Schaum and Scheidt¹⁹ is that crystallization, under the influence

TABLE 51.—INFLUENCE OF ELECTRIC FIELD ON CRYSTALLIZATION OF NITROBENZENE

Kilovolts.....	0.4	10-15	50	80
Time for crystallization at 0°.....	25 min.	9 min.	1-4 sec.	0.4 sec.

of the electric field, began in the middle of the solution rather than on an interface. This fact is attributed to the orientation of molecules by the action of the field on their dipoles.

The accelerating influence of Röntgen rays on formation of crystal nuclei of betol and santonine has been noted by Samuiacus.²⁰ Kondoguri²¹ has also observed that β rays from radium accelerated crystallization of supercooled piperine. Other rays had no effect.

132. Effect of Symmetry of the Molecule.—There is a great difference in the velocity with which various molecules crystallize. Compounds with a symmetrical structure crystallize relatively fast. In Table 52, the results of a number of experiments by Krah²² are recorded. His observations were made in glass capillaries, 75 cm. long and 1 to 2 mm. inside diameter. The time required for growth between two fixed points on the tube is taken as the velocity. Para-substituted benzene compounds, being very symmetrical, crystallize faster than the ortho, which, in turn, are faster than the meta isomers.

133. Equation for Velocity of Crystallization.—An equation¹⁵ which expresses the velocity of crystallization is

$$\frac{dC}{dt} = KS(C_s - C)$$

where C = the concentration of the solution at any time t .

K = a constant.

S = the surface area of the crystal or crystals.

C_s = the concentration of the saturated solution.

This equation is an adaptation of that of Noyes and Whitney²³ for the rate of solution of crystals in a solvent, and its applica-

tion to the phenomena of crystallization is based on the view that the processes of crystallization and of solution are exact reciprocals. The process is, therefore, a reaction of the first order and is dependent on the surface exposed for crystal growth

TABLE 52.—VELOCITY OF CRYSTALLIZATION OF A NUMBER OF *o*-, *m*-, AND *p*-ISOMERS

Compound	Melting point	Maximum velocity, m. per second
<i>o</i> -Dichlorobenzene.....	-17.6	2.2
<i>m</i> -Dichlorobenzene.....	-24.8	0.70
<i>p</i> -Dichlorobenzene.....	52.9	25.0
1,2,4-Trichlorobenzene.....	17.0	0.025
1,3,5-Trichlorobenzene.....	63.4	7.0
<i>o</i> -Dihydroxybenzene.....	104.0	1.7
<i>m</i> -Dihydroxybenzene.....	116.0	0.40
<i>p</i> -Dihydroxybenzene.....	169.0	6.3
<i>o</i> -Diaminobenzene.....	103.8	7.0
<i>p</i> -Diaminobenzene.....	140.0	10.0
<i>m</i> -Dinitrobenzene.....	89.7	6.0
<i>p</i> -Dinitrobenzene.....	172.1	15.0
<i>o</i> -Bromobenzoic acid.....	148.0	0.80
<i>m</i> -Bromobenzoic acid.....	153.0	0.255
<i>m</i> -Bromoaniline.....	18.5	0.048
<i>p</i> -Bromoaniline.....	66.4	1.6
Diphenylmethane.....	25.2	0.53
Triphenylmethane.....	93.1	0.027
1,2-Diphenylethylene.....	123.9	2.0
1,1-Diphenylethylene.....	8.2	0.016
1,2-Diphenylethane.....	50.8	0.70
1,1-Diphenylethane.....	-25.9	Less than 0.001
1,1,1-Triphenylethane.....	94.3	0.08
1,1,2-Triphenylethane.....	48.0	Less than 0.001

and the degree of saturation of the solution. The integrated form of this equation is

$$0.4343 KS = \frac{1}{t} \log \frac{C_0 - C_s}{C - C_s}$$

where C_0 = the initial concentration of the supersaturated solution.

Measurements of velocity were made by a refractometer which recorded a decrease in refractive index as crystallization proceeded. Table 53 illustrates the application of this equation to the crystallization of naphthalene at 0°C. from methyl alcohol at a constant stirring rate of 1,000 r.p.m. In the third column is a correction factor necessary to reduce the crystal surface

TABLE 53.—VELOCITY OF CRYSTALLIZATION OF NAPHTHALENE

Time, seconds	$C - C_s$	Surface correction factor	$K \times 10^3$
0.0	0.594	0.500	(75)
		0.71	
5.1	0.452	0.79	90
8.8	0.347		
		0.85	101
13.0	0.242		
		0.91	106
18.9	0.137		
		0.96	93
24.4	0.084		
		0.99	91
35.4	0.031		
		Average.....	96

to unit area. Agreement with experimental facts is very satisfactory.

The influence of small quantities of impurities (see also Sec. 123) on the velocity of crystallization of naphthalene from methanol solutions has been shown by Jenkins¹⁵ in a series of experiments which are tabulated in Table 54. Although these impurities had little effect upon crystallization of this substance, the action of collodion was more pronounced. The rate was inhibited strongly, and the process changed from first to one of second order.

When the foregoing equation was applied to the crystallization of lactose from water solution, it was found that the extremely slow velocity was tripled by the addition of a small amount of ammonia. According to Hudson,²⁴ this result is probably due to a catalytic action which hastens the formation of lactose hydrate. Other impurities, however, may cause a retardation in velocity

TABLE 54.—EFFECT OF IMPURITIES ON RATE OF CRYSTALLIZATION OF NAPHTHALENE

Added substance	Grams per 100 ml. of solution	Relative values of <i>K</i>
Control.....	1
Shellac.....	0.07	1
Sodium oleate.....	0.40	0.94
Picric acid.....	0.06	0.72
Methylene blue.....	0.062	0.88
Pontamine green <i>Gx</i>	0.0056	0.71
Quinine.....	0.125	1.13
Stearic acid.....	0.400	1.06
Potassium hydroxide.....	0.850	1.03
Urea.....	1.250	1.06
Iodine.....	0.146	0.76
Mercuric chloride.....	1.00	1.06
Colloidal calcium carbonate.....	0.010	0.77
Radium tube (inserted).....	1.03

134. Overcoming Difficulties in Crystallization.—The following illustrations, chosen at random, picture the difficulties sometimes present in crystallization. It should be noticed that the compounds were handled in such a way as to purify them or assist orientation or convert them to compounds that could be purified more easily. See also page 234.

Further heating under a high vacuum and rubbing with methanol until solidification occurred was the procedure necessary for crystallizing the oily product resulting from reaction of diphenylvinylmagnesium bromide and benzoylacetomesitylene.²⁵ Seeding a concentrated alcoholic solution of an amorphous residue obtained by evaporation of an ether extract from *Derris* root²⁶ yielded rotenone crystals. Purification by forming the picrate from which the pure hydrocarbon was regenerated was effective in the case of a resin obtained by selenium dehydrogenation of echinocystic acid.²⁷ The dark-red gum from deethylation of 1-eserethole methiodide was washed with ethyl acetate, dissolved in alcohol, treated with alcoholic picric acid, the solution charcoaled, decanted from the resinous deposit, and allowed to stand for 48 hr. in order to form crystals.²⁸ A brown tar, 17 g.,

containing an indole compound, was refluxed in 400 ml. of acetone with 2 g. of animal carbon for 2 hr., after which the solution was filtered and concentrated to a small volume. The residual pale-brown sirup became semisolid after standing several days.²⁹ Standing for a very long time—in fact for so many years that its exact history was not known—induced a sirupy sample of turanose, obtained from hydrolysis of melezitose, to crystallize. These crystals, in turn, were used to promote rapid crystallization by seeding a solution of the compound in hot methanol in which the sugar is moderately soluble.³⁰ Three weeks standing in methanol solution was necessary to obtain crystals of *d*-mannose diethylmercaptantetrabenzoate, which originally precipitated as a sirup by addition of petroleum ether to a chloroform solution.³¹ Scratching the sides of the test tube induced crystallization of retenediphenic acid which failed to congeal when kept in the icebox overnight.³² After a partially purified light-yellow oil, α -keto- δ -phenylvaleric acid, failed to crystallize, it was esterified with hydrochloric acid and alcohol, twice distilled, and the chief fraction saponified. The recovered keto acid crystallized on thorough cooling.³³ The active form of lactic acid melts at 52.8°C. Water is removed from the commercial grade by heating to 60° under a vacuum produced by a mercury diffusion pump. The temperature is then raised until the acid is distilled, using conditions which approximate those found in a molecular still. After two or three distillations, the solid compound collects in the receiver. It can be recrystallized from dry ethyl or isopropyl ether.³⁴ Inactive lactic acid melts at 18°.

135. In the successful *crystallization of rubber*⁴ the need for purity—freedom from nitrogenous compounds which might be adsorbed on the crystal nuclei—is emphasized. Fluidity must be adjusted so that the medium is mobile enough for formation of crystal nuclei yet sufficiently dilute for keeping the number of nuclei at a minimum, the purpose being to grow a number of large crystals rather than a crop of minute ones. The temperature should be low enough to start formation of nuclei and to provide for their subsequent growth. A solution of 1 part purified rubber in 2,000 parts ether at -65° separated tiny particles of rubber after about one hour. These particles grew slowly, and after 12 hr. the entire mass had settled as a clot.

At concentrations of 1 part rubber in 2,500, 3,000, and 3,500 parts solvent similar results were obtained but with increasing slowness. In these experiments the velocity of formation of crystal nuclei was too high for developing crystal habit. In other words an ideal temperature for formation is not identical with that for growth of crystals. The method finally employed was to support one Dewar flask in a larger one, which in turn was surrounded by insulating felt. Each flask contained acetone at -58°C . The flask containing the rubber solution was first cooled to -65° for 15 min. and then allowed to warm up to -58° before being set in the Dewar flasks. During a 24-hr. interval the temperature increased about 15° . Although the temperature rose, the velocity of crystallization was low, and a satisfactory degree of supersaturation was maintained. Rubber deposited on the sides of the tube in small nodules which under suitable conditions were half a millimeter or more in diameter. Purity, concentration, temperature, small increase in temperature, and time factors have all been carefully considered in this isolation of crystalline rubber. It is interesting to note that obtention of crystalline rubber was no accidental discovery but a result of strict adherence to the principles of crystallization as discussed in the excellent work of Tammann.³⁵

136. Fractionation by Crystallization.—Several methods are available for separating crystals by fractional crystallization. The solvent may be evaporated at a very slow rate by allowing the beaker, covered with a watch glass, to stand for very long periods. The mother liquor is transferred to another beaker at intervals, depending on the quantity and appearance of precipitate. Controlled evaporation in the absence of moisture from the air may be had by setting the beaker in a vacuum desiccator over some material which will absorb the solvent, *e.g.*, caustic alkali for acid solvents; calcium chloride for ketones, alcohols, esters, amines, etc.

A systematic scheme for separating mixtures may be necessary. Such a plan has been used in the isolation of rare earth salts³⁶ and is pictured, in a general fashion, in Fig. 75. The letter *c* represents crystals, and *l* shows the path of the mother liquor. The amount of solvent used in each crystallization should preferably be such as to permit half of the solid to crystal-

lize, leaving the balance in the mother liquor. Baxter and Behrens³⁷ used the same general method but employed a different system of recording when crystallizing lanthanum salts.

Miller and Adams,³⁸ searching unsuccessfully for reported optical isomers of 4,4-dimethyl-1-carboxycyclohexyl acetic acid, dissolved 0.15 g. of crude product in 1 l. of hot benzene. After evaporating to 600 ml., the first crop, consisting of 10 g., was

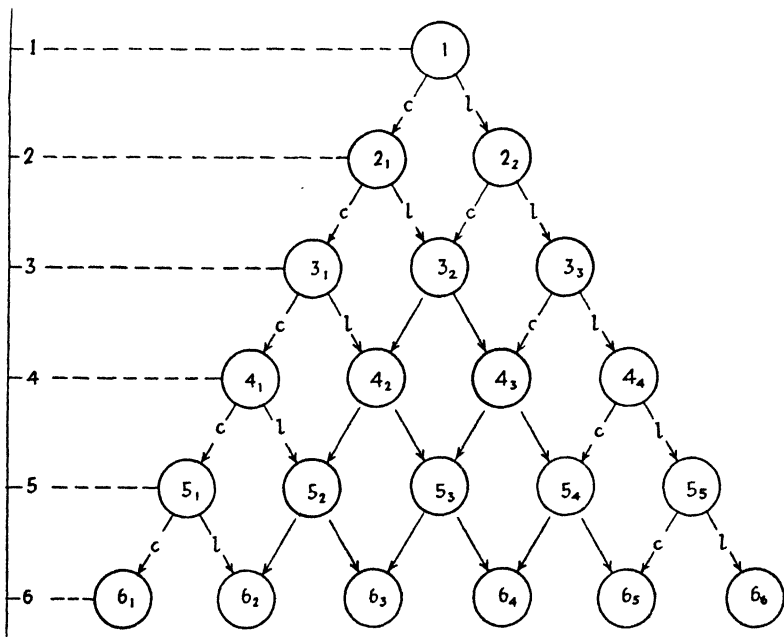


FIG. 75.—Scheme for systematic separation of compounds by crystallization.

converted to the anhydride and dissolved in 200 ml. of hot ligroin. The first crop of crystals from this medium, which we shall call solution A, was again crystallized from ligroin, giving fraction 1. The mother liquor from fraction 1 was combined with the second crop of crystals from solution A, and a crop of crystals (fraction 2) was obtained. The mother liquor from fraction 2 was then combined with the third crop of crystals from solution A; etc. This process, a standard procedure, was continued until nine fractions had been obtained. The melting point of the first was the same as that of the last.

Progressive addition of a diluent in which the compound is insoluble may also be used for fractional crystallization. Starting with a solution of a compound in alcohol, water may be added in graduated quantities to the mother liquor after each crop of crystals has been removed. The mixture is then warmed to effect solution and allowed to cool in order to obtain the next crop. The procedure is continued until the solid has been recovered in several batches of differing compositions. The same principle can be applied to progressive addition of petroleum ether or ligroin to solutions in organic solvents.

Cooling can also be employed in fractional crystallization. Solvents such as methanol, ethanol, ether, acetone, and equimolecular mixtures of carbon tetrachloride and chloroform, which do not crystallize at -78° , should be employed for this purpose. The solution is cooled to 0° to obtain a first crop of crystals. It can then be cooled to an arbitrarily determined temperature, such as -40° , followed by a final cooling to -78° . At this temperature nearly all of the remaining solid material will be stripped from solution.

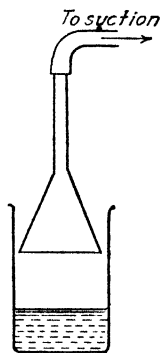


FIG. 76.—Anti-creeping device.

137. A very ingenious method for carrying out a *fractionation during melting* of a frozen mass was employed by Hicks.³⁹ The principle is to maintain the solidified material on a porous support in an insulated funnel so that the mother liquors containing impurity can drain from the mixture. The partly frozen mass is stirred as it melts, and the temperature is noted at regular intervals. The temperature rises gradually as impurities melt and drain into the beaker underneath the funnel. As soon as the substance becomes pure, the temperature remains constant during the remainder of the melting process so that the filtrate is of a reasonably high degree of purity. The method will not differentiate between eutectic mixtures and pure compounds. It has been successfully used in separation of pure paraffin hydrocarbons of low melting point. In the case of higher boiling fractions such as petroleum, wax, or oil use of a solvent is necessary.

138. Creeping.—Annoyance from creeping can sometimes be avoided by the device shown in Fig. 76 in which a gentle current of air sucked through the inverted funnel is often sufficient to hinder growth of crystals up the side of the container. Another method, if the solution is an aqueous one, is to cover the rim of the beaker by a thin coating of vaseline.⁴⁰ Covering the beaker with a cover glass is frequently all that is necessary.

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CHAPTER VIII

FILTRATION

139. Microfiltrations.—*Filtration in a capillary tube*¹ is necessary when only a few milligrams of a sample are at hand. A capillary tube 2 to 3 mm. in diameter and 8 to 10 cm. long is closed at one end. After introducing the sample and centrifuging to throw the material to the bottom of the tube a small constriction is made at *a* below the middle of the tube (see Fig. 77).



FIG. 77.—
Filtration
tube for
use with 2
to 3 mg. of
material.

Clean asbestos is pushed into the tube against the constriction and is held in place by a second constriction at *b*. A minute flame such as can be had from the tip of a piece of glass tubing drawn down to fine capillary dimensions is more than ample for making such constrictions even when the glass is pyrex. The upper end of the tube is next sealed, and the tube inverted and centrifuged. Such technique is very useful when handling small quantities of material (see Sec. 181 on micromanipulation). It may also be adapted to somewhat larger amounts using 4- to 6-mm.

glass tubing in place of capillaries.

140. Filter sticks are useful in handling small quantities. A sintered glass disk (Fig. 78) sealed on the end of glass tubing is lowered into a test tube, and the solvent removed by suction. With appropriate changes in construction, pressure can be substituted for suction. Many other tips which are adaptable for this same purpose are shown in Fig. 79. They are, in order, (a) a capillary tube, pipette, or any other tube with a small-diameter tip whose end is covered with a tiny piece of wet filter paper held in place by suction; (b) a tube with a constriction placed near one end so that asbestos fiber can be sucked against it after the general manner employed in construction of a Gooch-crucible mat with the exception that drying to constant weight is unnecessary; (c) filter paper wrapped around the smooth end of a

6- to 8-mm. glass tubing and held in place by a rubber band, string, or fine wire, a device that can be adapted to a considerable number of purposes; (d) a small funnel with paper or cloth held in place in a similar way; (e) a capillary tube with a constriction for holding a tiny asbestos plug after the manner described in the previous section, so that it can be used to filter the contents from another capillary tube containing 2 to 3 mg. of material, the filtrate being collected in the enlarged bulb (see also Sec. 181 on micro manipulation).

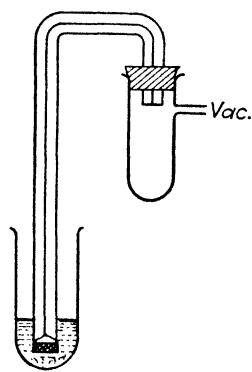


FIG. 78.—Filtration with a filter stick.

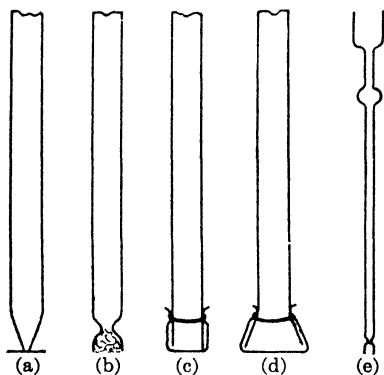


FIG. 79.—Tips for stick filters.

141. When *filtering a drop* of liquid on a microscope slide, it is customary to touch the drop with a hairlike capillary tube. The liquid is drawn up into the tube and may be transferred to another slide for further examination. A little suction may be applied, and the liquid collected in a small bulb from which the capillary protrudes. Where the mother liquor is no longer desired, the edge of the drop may be touched by a piece of filter paper.

142. It is always possible, of course, to *reduce the conventional type of filter* to a small scale so that quantities of 10 to 100 mg. may be easily handled. All operations such as continuous hot or cold filtrations, described in later sections of this chapter, can be carried out with a very small common filter by merely reducing the size of the respective parts. Loss of material is apt to be greater than results when filter sticks are employed.

143. Macro Filtrations.—The conventional apparatus is the funnel containing filter paper folded once at a right angle and a second time at slightly more than a right angle. Or the paper, after a half fold, is folded alternately back and forth a number of times in order to get a fluted effect and a consequent greater surface. Moderate suction can often be applied without danger

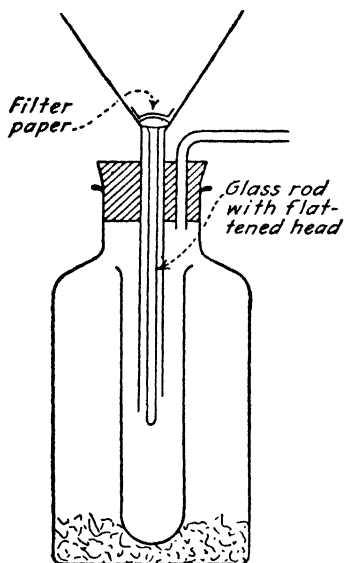


FIG. 80.

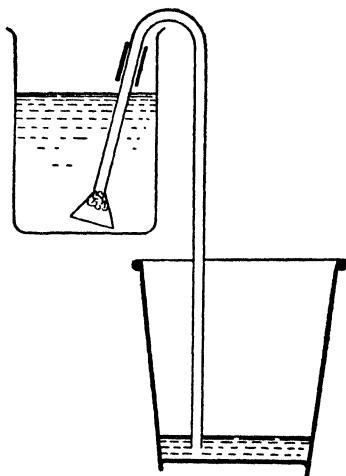


FIG. 81.

FIG. 80.—Methods of adapting the ordinary filter to use with suction.

FIG. 81.—Filtering large quantities of material with an inverted filter.

of breaking the paper. A convenient and useful laboratory unit may be assembled from a wide-mouth bottle or suction flask, a funnel, test tube, and rubber stopper. When the pressure becomes appreciable, a perforated platinum cone may be used as support for the bottom of the paper. Still another form of support is a glass rod with a flattened end, as shown in Fig. 80. In fact with such an inverted glass rod it is necessary only to use a piece of filter paper large enough to cover the bottom or to wrap a section of paper or a piece of cloth over the end and fit it into the funnel. Willstätter devised this simple glass nail for micro filtrations. Porcelain filter disks, covered with filter paper as suggested by Witt, may also be used to advantage.

Although the funnel is usually used in an upright position, it is by no means uncommon to invert it in a container so that large quantities may be filtered without the necessity of constant pouring (see Fig. 81). Cotton plugged into the stem or cloth or filter paper wrapped over the end and tied in place will serve as a filter under such conditions. Moderate amounts of suction can be had by varying the height of the siphon arm, and still more suction is attained by attaching the drain to the usual suction flask.

144. *Buchner funnels* are used regularly for filtrations under pressure. Owing to slight curvatures which are sometimes present on the plate it is often advisable to wet the paper first so that it will lie flat, then wash with alcohol, and next wash with the solvent being used in the solution. The funnels are supported on a suction flask by rubber stoppers or by thick flat pieces of rubber which rest on top of the flask. The latter have an advantage in that the stopper cannot be drawn down into the flask during filtration. Smith and Gring² have overcome the tendency of the ordinary rubber stopper to sink into the neck during filtration by turning the stopper inside out. The reformed stopper has the shape shown in Fig. 82, and its size is usually within 1 to 2 mm. of the original form. (See Table 55 for some exact dimensions.) With this type of stopper the funnel is held firmly in the suction flask and cannot be pulled inward. Heavy-walled suction flasks are standard equipment with Buchner funnels. In the case of large funnels the top-heavy arrangement, so apt to upset and cause breakage, can be avoided by supporting in a tripod (Fig. 83).^{2a} The funnel is then connected by pressure tubing to a suction flask, round-bottom flask, or bottle. Buchner funnels may also be inverted into a large volume of liquid in the same manner as described for ordinary funnels. In some cases it is possible and convenient to replace a Buchner funnel with a household article such as the upper part of a Silex coffee-making outfit.

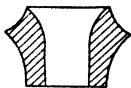


FIG. 82.—
Inverted rubber stopper for use in vacuum systems.

145. Filters made from *sintered glass*³ are especially useful in the laboratory because of the ease with which they can be cleaned, the resistance to corrosive liquids, and the many

TABLE 55.—SIZES OF INVERTED RUBBER STOPPERS USEFUL FOR BUCHNER FUNNELS, FILTERING CRUCIBLES, OR VACUUM DESICCATORS

Stopper number	Stopper diameter, mm.		Cork borer, diameter, mm.	Inverted stopper, mm.			
	Top	Bottom		Top	Middle	Bottom	Hole
13	70	60	43	57	75	63	42
13	70	60	35	60	76	59	34
12	64	58	35	53	70	53	34
11	56	50	35	45	60	53	35
10	50	42	35	44	52	45	34
10	50	42	28	42	55	43	25
9	45	37	28	35	47	39	27
9	45	37	25	35	47	40	23
8	40	32	25	35	44	37	23
8	40	32	28	32	43	36	27
7	37	30	25	31	40	33	23
7	37	30	28	32	40	32	33

uses to which they can be put. In addition to conventional filtrations, mention should be made of the freeing of mercury from dirt and amalgams by filtering through the coarser variety. Through the finer grades mercury will not pass, but gases will.

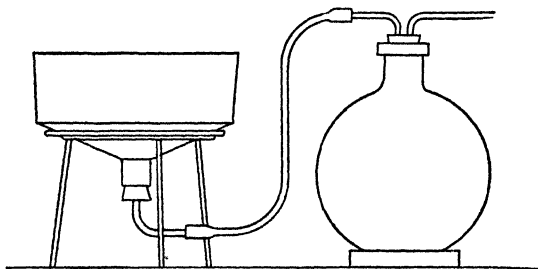


FIG. 83.—Filtration with a Buchner funnel and an ordinary flask.

Hence the filters can be used as safety valves in the manner shown in Fig. 84 or as traps to prevent sucking back of water from a water pump (see Fig. 85) or as substitutes for stopcocks⁴ where the grease of the latter might contaminate the liquid or gas (Fig. 86). Gases may be filtered through the disks. Explosions

will not pass through such a filter. Hence they can be used to protect the outlets of containers in which inflammable gases are

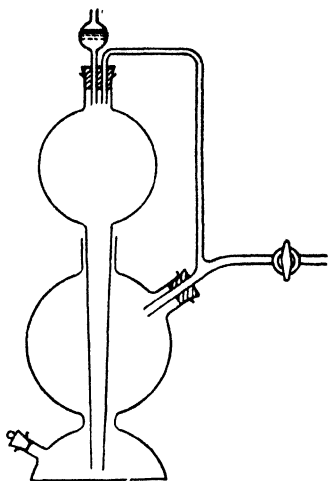


FIG. 84.

FIG. 84.—Sintered-glass safety valve in place on a Kipp generator.

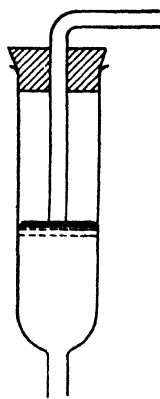


FIG. 85.

FIG. 85.—Sintered-glass-mercury safety valve to prevent sucking back of water from a water pump.

generated or stored. Intimate contact between liquids and gases occurs when the latter are admitted through a fritted-glass opening. For these purposes as well as many others, special forms are available commercially.

Commercial grades of sintered filters, a patented article, are made from Jena glass which cannot be sealed directly to pyrex. Suitable *methods for making filters* from pyrex have been described so that any research worker can make such pieces as he may need. Bruce and Bent⁵ ground scrap pyrex to the desired size and sintered it in a short piece of nickel tubing having an inside diameter of approximately 1 cm. The ring rested on a nickel plate about 2.5 cm. square. Sintering was effected by heating in a muffle furnace at a bright-red heat for about two minutes.

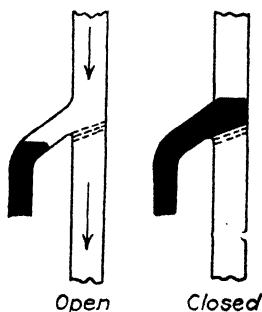


FIG. 86.—Mercury-sintered-glass valve for use on gas lines in place of a stopcock.

Cool and Graham,⁶ while constructing large aeration tubes, heated 80- to 100-mesh pyrex in a graphite mold at 1200 to 1400°C. for 30 to 40 sec., followed by reheating for 30 sec. more after removal of an inner core. Kirk, Craig, and Rosenfels⁷ used glass from the same lot of tubing into which the disk was to be sealed, ground it in an iron or agate (but not glass or porcelain) mortar, and sifted it through a 100-mesh sieve. It was then washed with strong acid to remove iron and with caustic solution if necessary to clean it. Grading of glass was not necessary for ordinary use but could be done in sieves or in an elutriator. For particles 100 to 150, 150 to 200, 200 to 275, and 275 to 325 mesh per inch the average sizes were 0.16, 0.08, 0.04, and 0.02 mm., respectively. Molds were constructed from two brass plates, each 0.8 cm. thick, the upper one having holes of the proper diameter and being held in place by two upright pins in the lower. Plate thickness was a little greater than that desired for the disk in order to allow for shrinkage. Moisture helped to pack the particles tightly in the mold. They were heated in a muffle furnace at 800° and were withdrawn from the mold as soon as cooled. Any discoloration was removed by carborundum paper. Sealing into tapered glass tubing helped prevent cracking of the finished product. The best seals were made by putting the tube in a lathe and pressing the joint with a carbon rod while applying a very fine hot flame. More recently Kirk⁸ has made small disks not larger than 15 mm. by blowing one end of a thick-walled capillary tubing into a bulb, filling it with ground glass, attaching the tube to a stirring motor, and heating the rotating bulb in a moderate air-gas blast flame (the glass should be scarcely red) for 10 min. The flame must be adjusted so that sintering is accomplished without fusion of the outer bulb. When cooled, the bulb is ground on a low-speed silicon carbide wheel to a desired thickness. If disks are to be used for spraying mercury into a cleaning tower, the mesh should be about 40.

Glass cloth, made by the makers of pyrex glass, is used commercially for filter mats. This material is very suitable for laboratory use. Owing to the readiness with which it fuses, direct seals to pyrex are impossible.

146. *Alundum filter disks* are not attacked by strong acid solutions (except hydrofluoric acid) but are affected by strong alkalis. They can be used in an ordinary 60-deg. funnel provided the edges are sealed with asbestos fiber or some cement. Their coefficient of expansion is near enough to pyrex glass to enable them to be sealed directly with careful annealing into the latter. Hence safety traps and gas filters can be constructed from these pieces as well as from sintered glass.

Alundum filter cones are made to fit into an ordinary 60-deg. funnel. A wide rubber band encloses the upper rim of funnel and cone. They offer a large filtering area, require no filter paper, and can be used with strong acids except hydrofluoric. When not in a funnel, the cones are set in wire (aluminum stands are furnished with the cones) stands so that precipitates can be dried and weighed without transferring or spilling. Such pieces of apparatus can often be used in place of more expensive Buchner funnels. For filtering larger quantities of material, alundum filter dishes which can be set into large funnels are available.

147. *Filter aids* are often necessary where liquids must be freed from all turbidity such as occurs with sugar solutions, fruit juices, or extracts of plant material. Silica gel, asbestos, Fuller's earth, filter cell, ground glass, sintered ground glass are frequently used. Hall and Baier⁹ put filter cloth in the bottom and then filled a Buchner funnel half full of alternate layers of a slurry of paper pulp and filter cell, care being taken to spread each layer evenly and to avoid compression of the pulp with too much suction. A small watch glass was placed on top to prevent damage to the filter bed from the inflowing liquid which itself contained filter cell. Only as much suction was applied as was necessary to maintain a continuous flow. When the filter became too full for convenient manipulation, it was sucked fairly dry, the top layer of pulp removed, and the filtration again started. It is not always necessary to have such a deep filter bed, addition of a filter aid to the solution, followed by a brief time of contact, and an ordinary filtration being alone adequate.

148. *Continuous filters* provide for filtering large quantities of material without manual attendance. The methods are quite simple and are illustrated by Fig. 87, showing (a) a bottle with a

siphon arrangement,¹⁰ (b) a separatory funnel with similar device, (c) a separatory funnel¹¹ with stem large enough to admit air into the funnel when the water level falls below the outlet, and (d) an inverted Erlenmeyer flask.¹² Continuous washing of precipi-

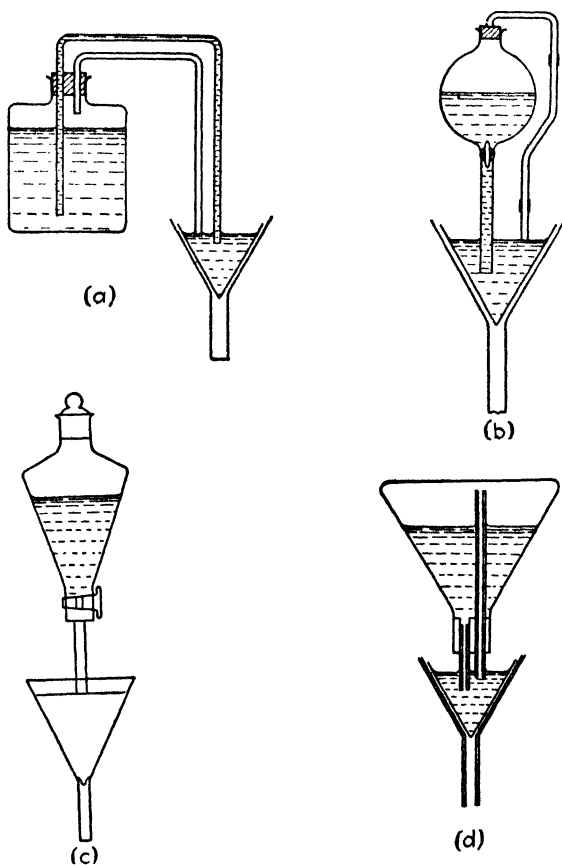


FIG. 87.—Automatic filtration apparatus.

tates is possible with the same types of apparatus as are employed for continuous filtrations.

149. Filtration of hot liquids can be carried out by putting the funnel in a steam cone (Fig. 88) or in a hot-water funnel, heated either with gas or with a resistance coil. A simple laboratory unit,¹³ based on the hot-water heater principle,

can be made from a bottomless bottle, a funnel, stopper, and tubing (8 to 10 mm.) as pictured in Fig. 89. Salt water (b.p. 108°) or calcium chloride solution (b.p. 180°) can be used if

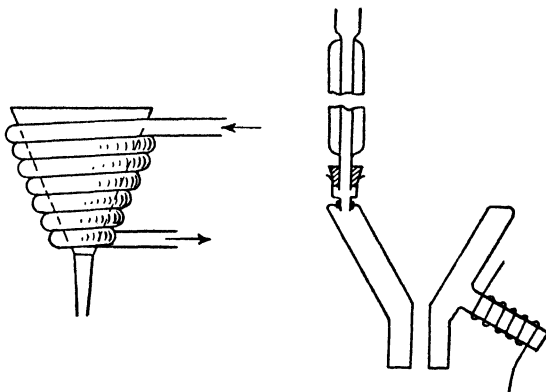


FIG. 88.—Steam cone and hot-water funnel with adaptor and reflux condenser for constant-temperature filtration with other bath liquids.

higher temperatures are wanted. Skau tubes (see Sec. 151) are useful for rapid filtrations of hot solutions where the quantity of material is limited. One of the simplest devices is an inverted-funnel arrangement as described in Sec. 142 or some form of a filter stick (see Sec. 139), but because rapid evaporation of solvent from a hot solution often breaks the vacuum it is frequently necessary to replace the water pump by one with a higher capacity, *e.g.*, a mercury-condensation pump. If the solution is in a flask, the necessary pressure can sometimes be obtained from vapors of the hot solution by passing an asbestos plugged stick filter through a cork and stopping the neck or raising the trap when ready to filter (see Fig. 90). The safety trap should be used with such an apparatus. Usually there is little danger of a clogged filter when immersed in a hot solution, so that with small quantities of solution the filter

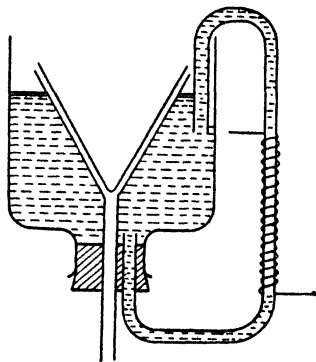


FIG. 89.—Apparatus for hot filtration.

may act as its own safety trap. Under no conditions, however, should a free flame ever be used with such an apparatus or, indeed, be near it. Goggles must also be worn.

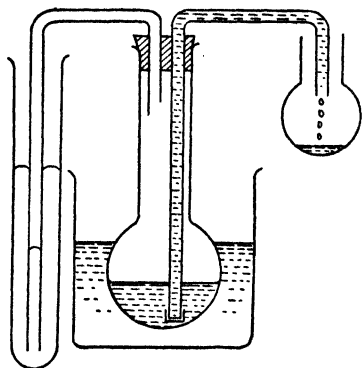


FIG. 90.—Method for hot filtration from a closed flask.

liquid. As mentioned before, small quantities of a cooled solution can be centrifuged in a Skau tube. Karrer and Schöpp¹⁴ spread a bed of solid carbon dioxide on the filter paper in a Buchner funnel in order to maintain a low temperature during filtration. Holmes and coworkers,¹⁵ in a similar way, filtered cholesterol from a pentane solution of the nonsaponifiable portion of halibut-liver oil. Filtration required only a few minutes. Carbon dioxide snow not only prevented warming of the solution but also provided an inert atmosphere for protection of the vitamin. Filtering by this method proved to be better than by use of a pressure bomb at 50 to 100 lb. of nitrogen. Attention might be called again to the usefulness of an inverted funnel or filter stick which need be immersed only in the beaker containing the chilled solu-

Hot filtration can sometimes be effected by placing the solid material on a Buchner funnel and pouring hot water over it. If the substance or impurity is an oil at that temperature, a rapid and convenient separation can be effected.

150. Low-temperature Filtrations may often be accomplished by replacing the liquid in a hot-water funnel with ice or a chilled

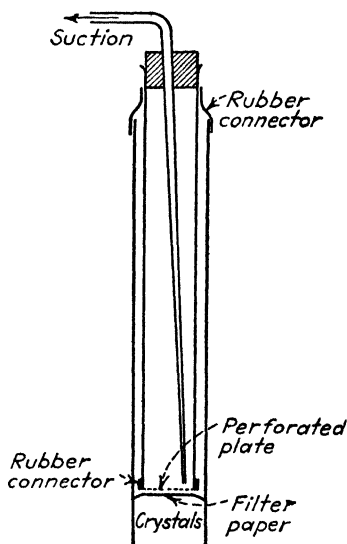


FIG. 91.—Dufraisse's apparatus for cold filtration.

tion. Dufraisse¹⁶ used a similar device (see Fig. 91) having two concentric tubes with annular space as small as possible, which could be immersed in a Dewar tube. If solid carbon dioxide has been added directly to a solution to be filtered, it is not possible, because of the escaping gas, to attain enough suction with the ordinary water pump to effect filtration. Resort must then be had to the larger capacity of the mercury-condensation pump (Sec. 98) or to a pressure filtration in a closed bottle after the manner described for hot filtrations and illustrated in Fig. 91. Care must again be taken that the flow of filtrate is rapid and continuous and that a safety trap be introduced if the quantity of solution is large or an adjustment of the rate is necessary.

151. The Centrifuge.—One of the most effective methods of filtering is by use of a centrifuge. Richards¹⁷ has pointed out that the force acting to drain and dry a precipitate is enormously greater by centrifugal than by gravitational draining. The value may be calculated from the formula

$$\frac{4\pi^2 n^2 r}{g}$$

where n = the number of revolutions per second.

r = the radius.

g = the gravitational constant 980.6.

If $n = 20$ (1,200 r.p.m.) and $r = 10$ cm., the drying is 160 times more effective than by gravity. He states that two crystallizations with the help of centrifugal separation and washing gave a product 2,000 times as pure as that obtained by gravitational draining. For attainment of an equal degree of purity the yield is about one hundred times as good by centrifuging as by draining.

Skau¹⁸ has devised a very convenient apparatus for laboratory use. His latest design, now available commercially, is shown in Fig. 92*a*. A filter paper, slit in the middle to allow passage of a wire, is pressed flat on a porcelain filter disk and folded over the edges. The disk is then pushed down upon the shoulder of tube *A*. The mixture to be filtered is put into *B*. Tube *A* with its porcelain filter plate is placed on top, and the whole is inverted, placed in a standard centrifuge tube, and whirled for a short time. The solid phase can be lifted out with the wire

Another tube¹⁹ in use in this laboratory is shown in Fig. 92b. It is modeled after Skau's earlier form but is designed to avoid breakage attendant on use of ground-glass joints. The substance is first placed in *B*; the porcelain filter plate (30 mm.) covered by filter paper is set on top, preferably with the beveled edge of the plate against the rim of the tube; the covering tube *C* carrying stopper and tube *A* is slid over the plate; and the apparatus is inverted and centrifuged. The bottom of tube *C* is made as flat as possible, and the rubber stopper should have a generous section cut out to allow escape of air from the lower compartment. It can be used at 1,500 r.p.m. without danger of breakage.

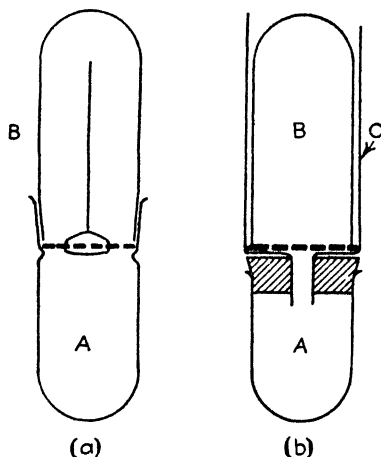


FIG. 92.—Skau tubes for use in a centrifuge.

These tubes are especially useful for rapid filtrations of compounds that are not gummy. Skau originally employed them for filtering crystals of low-boiling liquids such as pentane, which could be frozen at liquid-air temperatures and then centrifuged. The rapidity of the latter process made it possible to effect filtration before melting. So rapid and complete are the Skau tubes in separating many solids from liquids that they can be used for construction of freezing-point diagrams of sufficient accuracy for many needs. Instead of the conventional manner of determining the freezing point of a given composition, the composition of the mixture having a given freezing point is determined. A mixture of known composition is put into the tube and immersed (usually enclosed in a rubber toy balloon or larger glass tube) in a thermostat whose temperature is at the desired point. When equilibrium has been attained, it is centrifuged, and the proportion of solid and liquid found. Since equilibrium conditions were attained, the temperature at which the mass was kept represents the freezing point of the liquid

phase. This fact is true only if there has been no temperature change during the process of filtration. Because only 20 sec. is required for this step the assumption appears to be a reasonable one. Calculation of the composition of the liquid phase is made by means of the formulas

For A :

$$\frac{a}{a + b - s_b},$$

For B :

$$\frac{b - s_b}{a + b - s_b},$$

where A and B = the two components for which a and b are the respective quantities.

s_b = the grams of solid B which are separated by centrifuging.

After the determination, liquid and solid portions are combined and frozen at a different temperature. Separation by centrifuging and determination of the respective amounts gives another point on the freezing-point diagram. The operation can be repeated to complete the diagram, or fresh samples can be used for each determination. If the solutions are perfect, either A or B crystallizes out in substantially pure form, depending on which side of the eutectic composition is being studied. The eutectic composition and temperature themselves can be determined provided one constituent is a solid at room temperature. A mixture, say, of an equal number of mols of A and B is cooled until it is entirely solidified. It is then centrifuged and allowed to warm. The eutectic composition, having a lower melting point than any other mixture, is thrown out of the solid until only the pure compound melting above room temperature is left. The composition of the eutectic solution in the filtrate is then calculated from the total weight and the weight of solid. The freezing point of this eutectic can be determined very simply by means of a cooling curve, since it will remain constant during freezing. In Table 56 the results of Skau and Rowe for a mixture of benzene and naphthalene are given. Best agreement with theoretical values (taken from the International Critical Tables) was found when the quantities of solid and liquid phase

were approximately equal. The accuracy of the method is from 2 to 4 per cent.

TABLE 56.—BENZENE-NAPHTHALENE SOLUBILITY AS DETERMINED BY CENTRIFUGING

C ₆ H ₆ , grams	C ₁₀ H ₈ , grams	C ₆ H ₆ , Mol fraction	Temp. before centri- fuging °C.	Mother liquor, grams	Mol fraction of benzene in mother liquor		
					Expt.	Theoret.	Diff.
5.29	21.15	0.291	12.8	7.40	0.804	0.788	+0.016
7.272	7.868	0.603	-10*	9.155	0.864	0.875	-0.011
7.272	7.868	0.603	25.5	12.285	0.704	0.700	+0.004
3.985	7.885	0.453	-14*	4.645	0.908	0.875	+0.033
3.985	7.885	0.453	50.5	10.285	0.509	0.454	+0.055

* Determination of eutectic composition. The eutectic temperature was -3.5°C.

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CHAPTER IX

ADSORPTION

152. Processes involving adsorption include decolorization with carbon or other material and purification by chromatographic adsorption. The former is one of the time-honored methods of removing colored impurities. The method by which it operates is not always considered carefully by the organic chemist, so that failure to secure a desired action is blamed entirely on the grade of carbon employed. Some of the basic principles governing adsorption on carbon are therefore restated in this chapter to the end that its limitations and use may be understood.

Closely allied with adsorption on carbon is the phenomenon of chromatographic adsorption. Of late years it has become one of the important methods of purification. Indeed, in many cases it is the only method of obtaining certain natural products in the pure state. It differs from decolorization on carbon chiefly in that a white or light-colored adsorbent is commonly used, and the experimental conditions are adjusted to permit adsorption in colored bands. Enough applications of the process will be discussed in detail to give a clear understanding of the method.

DECOLORIZATIONS WITH CARBON

153. Sources of Carbon.—Activated charcoal is commonly made¹ by heating wood at relatively low temperatures, *e.g.*, at 900° for 12 hr., in order to carbonize it. It is then ground and heated with steam at about 950° for 7 hr. This last process is essential. It is the activating step in which air, adsorbed during cooling, together with steam drives out hydrocarbons formed by carbonizing. Air may be used as the activating agent at 350 to 450° but is apt to cause excessive consumption of carbon. The steam treatment at 800 to 1000° makes a more active surface. In

studies by Ockrent² the carbon was made by burning 2 kg. of saccharose (yield 350 g.), degassing at 500° for 3 hr. under vacuum, and then burning with purified oxygen at 500° for 2 hr. at the rate of 20 l. of gas per hour.

Barker³ concludes that activation is accompanied by a marked increase in the hydrogen and oxygen content of charcoal, that the primary carbon is partially converted to graphite particles which are extremely small and have a large surface energy due to loosely bound electrons on the graphite surface, and that the interior surface area is increased. Presence of graphite in active carbons may, indeed, be of first importance. Wolf and Riehl⁴ point out that very finely divided graphite has been shown to have an adsorptive power nearly equal to that of active carbon. Free valence bonds at the crystal surface of graphite seem to have an important role in these processes, since photographs⁵ of graphite platelets which have been exposed to radium emanations show denser adsorption at the edges than at the center.

Carbon made in the preceding manner has replaced in many instances the familiar bone char. Indeed, the superiority of some commercial wood carbons (see Table 58) has been very marked. The theory underlying the action of bone char differs in no way from that of activated carbons.

154. Nature of Substances Adsorbed.—Practically all types of organic compounds as well as inorganic are adsorbed on carbon. Michaelis⁶ states that there are only two exceptions known, the sulfates of the alkali metal and glycine. It behooves the organic chemist, therefore, to use discretion in the quantity of carbon used, lest the agent remove the desired product along with impurities. Fortunately, colored impurities are usually very complex and are preferentially adsorbed. Very little loss need occur if care is exercised in the amount added, if proper digestion to obtain equilibrium conditions with each added portion is made, and if simple tests, such as are possible by a micro filtration or withdrawal of a sample with a filter stick, are performed to indicate when the end of the process is reached.

155. Effect of Solvents.—Solvents have a profound effect on the amount of substance adsorbed. In a study of adsorption of caprylic acid (15 ml. of a 0.01-molal solution) on carbon

(1 g.), Nekrassow⁷ found that the percentage adsorbed varied from 17 to 78 depending on the solvent used (see Table 57).

TABLE 57.—ADSORPTION OF CAPRYLIC ACID ON CARBON IN VARIOUS SOLVENTS

Solvent	Percentage Adsorbed
Ether.....	17.2
Acetone.....	20.9
Chloroform.....	22.0
Ethanol.....	34.3
Carbon tetrachloride.....	56.9
Methanol.....	59.6
Toluene.....	61.0
Benzene.....	68.8
Petroleum ether.....	72.0
Carbon disulfide.....	78.2
Water.....	78.4

Sata and Kurano,⁸ from experiments on adsorption of dinitrobenzenes, nitroanilines, and nitrophenols in carbon tetrachloride, acetone, and benzene, concluded that the less the solubility the greater the adsorption. Roychoudhury,⁹ however, could observe no exact relationship between adsorption and insolubility of various acids in water. These facts, while they may not point to an exact relationship, do nevertheless show that widely different results may be obtained, depending upon the solvent employed. In general, a decolorization process should be carried out in a solvent in which the impurity is only slightly soluble. Failure to decolorize a compound should always be examined from this point of view, and a change made to a poorer solvent before use of carbon is abandoned.

156. Effect of pH of Medium.—As would be expected from the electrical nature of an adsorption process, the phenomenon is influenced in a large number of cases by the pH of the medium. Positively charged substances¹⁰ such as methylene blue are adsorbed best from alkaline solution, but caramel or benzoazurin, being negatively charged, are adsorbed best from acid media. Differences in efficiency of carbon under varying pH conditions are clearly illustrated (Table 58) by results with benzoazurin in water solution (0.08 per cent concentration) at different initial pH values where the decolorizing efficiency falls off sharply with

TABLE 58.—EFFICIENCIES OF VARIOUS CARBONS IN DECOLORIZING OF BENZOAZURIN SOLUTIONS

Initial pH	Percentage benzoazurin removed by			
	Bone black	Darco	Norit	Superfiltchar
0.65	87.4	94.3	
1.49	95.7	75.9	57.5	94.8
2.18	69	57.5	46.0	74.3
3.57	23.1	47.4	29.6	24.9
5.43	17.4	43.1	29.1	19.3
6.56	17.4	42.9	28.6	20.0
7.77	16.7	42.2	27.0	16.0
8.13	17.4	42.2	28.1	16.0
8.25	16.7	41.2	28.6	16.7
10.80	5.8	41.2	25.9	0.0

decreasing acidity. Amphoteric substances such as proteins have been found to be adsorbed best in a region of pH 3 to 6. Adsorption of the nonelectrolytic substance dextrose is not affected by the pH.

157. The Equation for Adsorption.—Langmuir¹¹ has proposed an equation by which the amount of adsorption may be expressed. If Γ represents the number of molecules adsorbed per unit area; Γ_{\max} , the number of adsorbed molecules in a saturated layer at the surface, the relationship is

$$k\Gamma = C\left(1 - \frac{\Gamma}{\Gamma_{\max}}\right)$$

where k = an equilibrium constant.

By applying this equation to the adsorption of acetic and of salicylic acids on four different grades of sugar carbons of widely varying efficiencies, Ockrent² finds that the same value of k is obtained in each series (see Table 59). This result would not have been expected had the carbons possessed different surface structures. Difference between carbons is attributed, therefore, to difference in porosity. The column A/M tabulates the number of carbon atoms per each molecule adsorbed. Thus, in carbon A one molecule of acetic acid was adsorbed for every 62 atoms of carbon present. The amount of adsorption of

salicylic acid is less, a fact that would be expected from the view that adsorption of carbon compounds on carbons occurs because of attachment of carbon to carbon, not of polar groups to carbon. Salicylic acid, for example, is pictured by Ockrent as lying flat on the carbon with its polar groups oriented toward the aqueous phase.

TABLE 59.—CONSTANTS OF ADSORPTION ON CARBON FOR ACETIC AND SALICYLIC ACIDS

Carbon	Acetic acid			Salicylic acid		
	Max.	<i>k</i>	<i>A/M</i>	Max.	<i>k</i>	<i>A/M</i>
<i>A</i>	1.33	0.70	62	0.476	0.031	172
<i>B</i>	1.00	0.70	82	0.521	0.030	157
<i>C</i> ₁	0.80	0.71	102	0.602	0.033	136
<i>C</i> ₂	1.11	0.70	74	0.893	0.027	92

158. Manner of Adsorption.—As stated in the previous section, adsorption is apt to occur because of attraction of carbon to carbon. Traube's rule, in fact, is that the adsorption in a homologous series varies directly with the number of CH₂ groups. That is to say, the greater the number of methylene groups in the molecule the more firmly is it adsorbed. This rule does not always hold for higher members of a homologous series, a fact attributed by some workers to smallness of the pores into which the large molecules cannot enter.

159. Application of Carbon to Decolorizations.—Assuming that the progress of decolorization is followed by simple tests as indicated in Sec. 154, it follows from the foregoing considerations that difficulties arising in decolorizing organic compound may not always be due to the grade of carbon being used. Carbons do vary greatly in their activity, and cases may arise that require the research worker to activate his own carbon. But we have seen that the difference may be one of degree and not of kind. Failure to function properly may often be due to factors other than the particular carbon employed. The acidity or basicity of the medium and the nature of the solvent are of prime importance. Use of a solvent in which the material is less soluble is often the solution of the trouble. In cases where the product

is lost during decolorization, change to a better solvent must be tried. If the compound is sensitive to moisture, the carbon must be dried, a step that can be carried out conveniently by adding xylene and distilling until the distillate runs clear. Where compounds are affected by the presence of air, the carbon must be degassed and filled with hydrogen or nitrogen or boiled in the solvent to be used until free from air. Spent carbon should not be thrown away until isolation of the desired product is assured.

160. Decolorization with Other Substances.—Carbon is not the only material that can be used as a decolorizing agent. The familiar spreading of a semicrystalline mass on a porous tile effects removal of colored as well as of oily substances. A few drops of solvent added from time to time aids the process by keeping the material moist. Use of a porous plate, which is apt to be wasteful, can usually be avoided. But almost any material will preferentially adsorb colored compounds. Indeed, the whole process of chromatographic adsorption, to be described in the following sections, is, in reality, a decolorization of a solution. There is no reason why the methods used in such a field cannot be applied in many cases to the ordinary processes of decolorization so long considered a function of carbon.

CHROMATOGRAPHIC ADSORPTION

161. General Principles.—When a solution of a colored compound is passed through a tube containing a colorless or light-colored solid, the compounds are adsorbed in the order of their affinity for the agent, so that colored bands, called chromatograms, develop in the tube. These bands may be discernible only under ultraviolet light. The tubes are next washed with a portion of solvent in order to sharpen the boundaries between colored sections and remove mother liquor. This action is called developing, and the solvent is called a developing solvent. The tube is then cut into sections or otherwise divided at the color boundaries, and the colored compounds recovered with a good, hot, or wet, solvent. This recovery is called elution or elutriation. It is obvious that chromatographic adsorption is but a division of the general problem of adsorptions. For the organic chemist it has become one of the most important

tools in purification, whose usefulness has just begun to be realized.

162. Adsorbents.—Any light-colored solid may be used as an adsorbing agent. Activated alumina is one of the most common. Oxides, carbonates, or sulfates of magnesium, calcium, or barium are frequently used. Sodium sulfate is also satisfactory. Siliceous material such as talcum, Fuller's earth, filter cell, pumice, floridium, silica gel, or powdered glass may be employed. Sugar is not so good as alumina but is easy to remove because of its solubility in water. Carbon has also been used. A wide choice of adsorbents is therefore possible, and one may be selected either by trial and error or by a choice based on the basic, acid, or neutral character desired. The quantity employed varies with its porosity and adsorption affinity. Hesse¹² gives the following table of values. Effectiveness of many agents can

TABLE 60.—QUANTITIES OF ADSORBENT FOR 1 G. OF DIFFERENT ORGANIC COMPOUNDS

Compound	Adsorbent	Grams of adsorbent
Carotene.....	Fuller's earth	2,000
Lutein.....	Alumina	5,000
Chlorophyll.....	Sugar	1,000
Anthracene.....	Alumina	50
Bufotalin.....	Alumina	60
Cholesterol.....	Alumina	20

be improved by heating in a vacuum oven at 150° and cooling in a desiccator prior to use.

163. Solutions.—In general, adsorption will be more complete the less the solubility of the compound in the *solvent*. Thus, petroleum ether or ligroin is a favorite solvent in a large number of cases. Adsorption will occur, however, from benzene, alcohol, ether, or other solvents. Ruggli and Jensen,¹³ for example, have shown that dyes may be chromatographically adsorbed on alumina from aqueous solutions. For elution one chooses a better solvent, a hot solvent, or one that contains some water. Many adsorbents, such as activated alumina, are dehydrating agents or have a high affinity for water. Hence a wet solvent

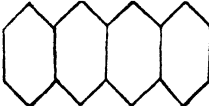


will permit an exchange of colored compounds for water. In other cases the presence of an acid or base may effect liberation of adsorbed material. In general, the conditions for removal are the reverse of those for adsorption, and the same principles which were discussed in the sections on decolorization by carbon are applicable to problems arising in chromatographic adsorption.

For different *solutes* within a given series strength of adsorption increases with number of double bonds. Carotenes,¹⁴ for example, are adsorbed in order according to the number, as well as position, of double bonds in the molecule. Adsorption of diphenylpolyenes, shown in decreasing order of strength in Table 61, is also in accord with that expected from the number of double bonds. Two different yellows and three different blues result.

TABLE 61.—EFFECT OF NUMBER OF DOUBLE BONDS ON ADSORPTION OF SOME POLYENE COMPOUNDS


Formula	Compound	Color of chromogram
$C_6H_5(CH=CH)_4C_6H_5$	Diphenyloctatetrene	Yellow
$C_6H_5(CH=CH)_3C_6H_5$	Diphenylhexatriene	Yellow
$C_6H_5(CH=CH)_2C_6H_5$	Diphenylbutadiene	Blue
$C_6H_5CH=CHC_6H_5$	Stilbene	Blue
$C_6H_5C_6H_5$	Diphenyl	Blue

TABLE 62.—ADSORPTION OF SOME AROMATIC HYDROCARBONS

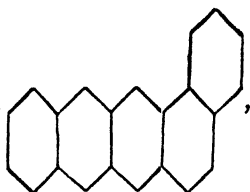
Formula	Compound	Color of chromogram
	Naphthacene	Weak Yellow
	Anthracene	Blue Fluorescence
	Naphthalene	Not Adsorbed

The order of absorption of some aromatic hydrocarbons, shown in Table 62, is in agreement with the same principle.

But structural influences are also pronounced. Thus, naphtha-

cene, , is adsorbed as an orange-red layer more

strongly than is 1,2,6,7-dibenzanthracene,



whose chromogram is yellow, although the former has fewer double bonds. This behavior suggests that the greater tendency of linear benzanthracenes to exist as diyls and to have greater color may have some bearing on ease of adsorption. Further increase in angular structure, such as is found in the cancer-producing hydrocarbon 1,2,5,6-dibenzanthracene, is accompanied by still weaker adsorption.

All manner of colored compounds are adsorbed; chlorophylls, carotenes, vitamins, hydrocarbons, and dyes are susceptible to the sensitive nature of this method, which depends upon slight difference in residual affinity of the adsorbent for materials with which it is contacted. Usually adsorption is greater the deeper the color, the more the unsaturation, the larger the molecule, and the stronger the polarity (alcohol > ketone > ester > hydrocarbon).

164. Apparatus and Manipulation.—The parts of an apparatus (see Fig. 93) are a tube, narrow and tall rather than wide and short, which has its lower end covered with a wire-gauze cup or indented sufficiently to support a little cotton which, in turn, supports the column of adsorbent; a dropping funnel attached by a stopper to the upper end of the tube; an adaptor which fits over the bottom of the tube and has a closely fitting wire gauze to support the copper-gauze cup, but which may be dispensed with if indentations or other obvious arrangements have been made to support the column; and a suction flask. Banding is more uniform and easier to observe the smaller the tube diameter. The adsorbent, preferably ground to a uniform

mesh, can be added dry or wet. Winterstein and Stein used a suspension of the material in ligroin or petroleum ether which settled in fairly uniform layers. Strain packed the adsorbent while dry by pressing it with a rod. During the experiment the height of liquid above the packed section should be enough to prevent dislodging of adsorbent by the entering stream. Gentle suction, 680 mm., is sufficient. A high vacuum causes packing

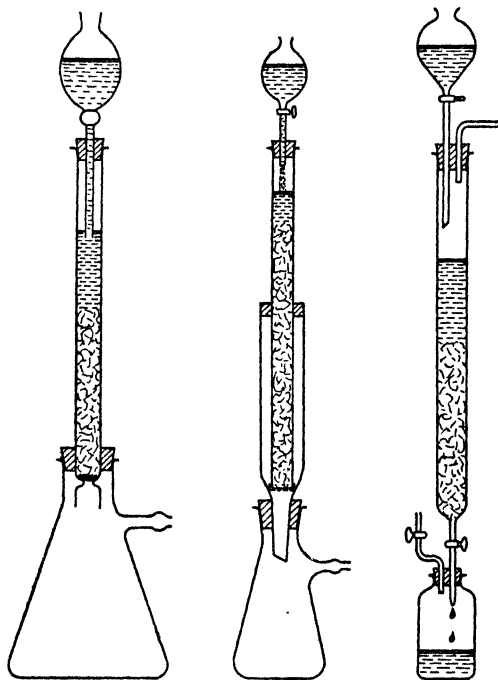


FIG. 93.—Apparatus for chromatographic adsorption.

of adsorbent as well as evaporation of solvent in the lower end of the column.

It is advisable sometimes to wash the column with 200 ml. or more—the quantity depending on the size of the tube—of pure solvent before addition of the solution in order to remove any material that may have been on the adsorbent. The solution is then allowed to filter through the column. As the last portion leaves the separatory funnel, the developing solution is added. After filtration is complete, the contents are dried

in air or nitrogen, and the tube cut into sections at the boundaries of the colored zones. Or the tube may be freed of its contents by a plunger which pushes out the dried material so that the colored zones may be separated as they leave the tube. The product is then recovered by digestion with a solvent containing water or with a better solvent than was employed in the adsorption. Where the material is sensitive to air, the whole operation must be conducted in an inert atmosphere. For large quantities of material Winterstein and Schön used a glass cylinder 50 cm. high and 12.5 cm. in diameter with a ground flange on the lower end (see Fig. 94). This tube rested on a Porolith filter plate

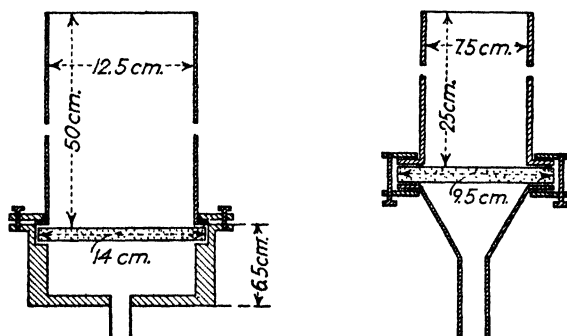


FIG. 94.—Apparatus of Winterstein and Stein for chromatographic adsorption of large quantities of material.

surrounded by a rubber ring which, in turn, was in a metal case having an outlet at the bottom for attachment to a flask. A metal ring above the glass flange, with screws connecting it to the metal case, held the glass tube firmly. A somewhat similar but smaller arrangement was made in which the metal case was replaced by a funnel with flanges. The same investigators adapted a percolator to the work.

165. Applications.—The method was first applied by Tswett¹⁵ (it is often referred to as Tswett's process) to the separation of chlorophyll. By filtering a carbon disulfide solution through a tube containing calcium carbonate, he showed that a substance phaeophytin (from the action of oxalic acid on an alcoholic solution of chlorophyll) was, in reality, a mixture of α - and β -chlorophyll. Some data from extensive experiments by Winterstein and coworkers are collected in Table 63.

TABLE 63.—CONDITIONS IN ADSORPTION OF SOME COMPOUNDS

Substance	Solvent	Adsorbent	Tube size, height \times diam., cm.	Solvent	
				Developing	Elutriating
Hydrocarbon fraction from carotene.....	Benzine	Activated alumina	10 \times 1	Benzine-benzene mixture 9:1	Methanol-benzine
Xanthophyll	Benzine	Calcium carbonate strongly dried	12 \times 3	Benzine	Methanol-benzine
Carotinoids.....	Benzine	Activated alumina	30 \times 2	Petroleum ether	Methanol-benzine
Ergosterol-cholesterol mixture 0.59 g	Benzene-hexane 1:1; 150 ml.	Alumina-Fuller's earth 5:1	14 \times 2	Benzene-hexane 1:1; 150 ml.	Ether-methanol
Cholesterol-ergosterol 20, g.....	Benzene-hexane 1:1; 200 ml.	Activated alumina	15 \times 5.5	Benzene-hexane 1:1; 500 ml.	Ether-methanol
Geraniol-limonene 1:1, 8 g.....	Benzine 700 ml.	Activated alumina	6 \times 1	Benzine 300 ml.	Petroleum ether- methanol
Hentriacontane-dipalmitylketone	Benzine	Alumina Fuller's earth	6 \times 1	Benzine	Petroleum ether- methanol
Chlorophyll A-chlorophyll B, 3:2, 4 g.....	Benzine-benzene 14:1; 200 ml.	Powdered sugar or sugar-talcum 6:1	85 \times 12 (percolator)	Benzine-petroleum ether	Ether-acetone 1:1
Chlorophyll 1 g.....	Benzine-benzene 4:1; 2 l.	Powdered sugar	50 \times 12.5	Benzine	Benzine-methanol

Karrer and coworkers¹⁶ adsorbed vitamin A and carotenoid pigments under an atmosphere of nitrogen on calcium oxide, hydroxide, or carbonate. Holmes and coworkers¹⁷ used carbon and magnesia as adsorbents for the vitamin. The latter group of investigators elutriated by washing the entire column with suitable solvents, so that solutions with varying degrees of potency were obtained. The less strongly adsorbed materials were removed first, followed by more strongly adsorbed fractions. Strain¹⁸ has adsorbed carotenes on magnesium oxide. He also found that xanthophylls could not be differentially adsorbed on magnesia from petroleum-ether solution but could from dichloromethane or dichloroethane solutions. Dyes have been adsorbed on alumina by Ruggli and Jensen.¹³ High-molecular-weight hydrocarbons have been purified by a number of experimenters. Diels and Rickert¹⁹ dehydrogenated cholesteryl chloride with selenium and obtained a beautifully crystalline product. In spite of its appearance, it contained an impurity which was most difficult to remove by ordinary means. It was finally purified by dissolving 2.8 to 3 g. in 80 to 95 ml. of petroleum ether (15 to 20°) and adsorbing on activated alumina in a tube 2 cm. wide and 20 to 22 cm. deep. A light vacuum was used to aid the filtration. Elution was accomplished by more solvent, and the whole process repeated with a newly filled tube in order to remove all trace of impurity. A yield of 1.8 to 1.9 g. of pure sterin, $C_{18}H_{16}$, was obtained. Strain separated colorless ketones by converting them to colored nitro- and dinitro-phenylhydrazones which were then adsorbed on alumina. Karrer and Strong²⁰ adsorbed paeonins on alumina from water solutions obtaining purple and bright-blue zones.

The foregoing collection is sufficient to illustrate the utility of the method as a means of purification and separation. For other reviews of the subject reference can be had to Ruggli and Jensen, to Hesse, and to Zechmeister and Chohnoky.²¹

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CHAPTER X

EXTRACTION

166. Extraction is one of common methods employed in the laboratory for obtaining and purifying materials. In its simplest form the process consists of shaking two immiscible solutions in a separatory funnel, separating the two phases, and recovering the desired material. But many other factors must be considered. For example, this process might be continued an indefinite number of times with ether in contact with an aqueous solution of oxalic acid, with no appreciable transfer of acid from the aqueous phase, whereas a change to ethyl acetate would permit a prompt extraction. Solvent effects must be considered even in continuous extractions. Systematic extraction often affords a simple and convenient method of separation where other means are very difficult. Continuous-extraction apparatus is of great importance as a method of getting natural products. These interesting aspects relating to extraction are discussed in this chapter.

167. Single Extraction. *The Amount of Extracting Solvent.*—The formula that expresses an extraction process is

$$X_n = X_0 \left(\frac{KW}{KW + L} \right)^n$$

where W = the volume of the solution in milliliters.

X_0 = the grams of dissolved substance.

L = the volume of extracting solvent in milliliters.

K = the distribution ratio of the substance between the two solvents.

X_n = the weight of substance remaining after the n th extraction.

By this formula it can be calculated that it is more efficient to divide the extracting solvent into several small portions than to make a single extraction with the whole quantity.

168. Effect of Solvents.—The most common laboratory extraction is that done in a separatory funnel. A solution, usually aqueous, is subjected to one or repeated single extractions with an organic solvent in order to remove organic compounds. The ease with which this separation can be accomplished depends upon solubility of the substances concerned in the respective solvents. Compounds that are relatively insoluble in water may be removed by petroleum ether or ligroin; if more soluble in water, by benzene or ethyl ether; if very soluble in water, by ethyl acetate. The last solvent may be employed even when the aqueous solution is strongly alkaline, provided the time of contact is not excessive. Saturating the aqueous layer with salt is a pronounced aid for rapid extraction. Valuable products are often overlooked because extraction of water-soluble substances is not completed.

169. Effect of Hydrolysis of Salts.—Interesting results are sometimes secured in extraction of salts that are greatly hydrolyzed. Vavon and Zaharia¹ in studying the separation of neutral products from phenols by extraction from alkaline solution observed that considerable amounts of the latter were also extracted. When a 10-ml. solution of 0.01 mol of phenol, neutralized by an equivalent amount of alkali, was shaken with 20 ml. of ether for about 10 min., the amount of phenol removed was 7.5 per cent. Values for a number of phenols tested in like manner are given in Table 64. These extractions are due to hydrolysis of sodium phenate. Excess of alkali diminishes the amount extracted, but changing the solvent is also helpful. Thus in the case of thymol the amounts extracted by different solvents are: ether, 88; benzene, 38; carbon tetrachloride, 25; and petroleum ether, 22 per cent. These solvents are in the order of decreasing solubility of thymol in water. Abietic acid² can be extracted by ether from a solution of sodium abietate, but other sodium soaps are not so decomposed. When 200 ml. of a 0.1-molal solution of triethanolamineoleate was extracted with three successive 50-ml. portions of ether by shaking for 2 min., and the composite ether extract was washed three times with 20-ml. portions of water, the amount of oleic acid found in the ether layer was 58.5 per cent of the original amount present in the triethanolamineoleate, but less than 0.1

TABLE 64.—PERCENTAGE OF PHENOL EXTRACTED BY ETHER FROM AN AQUEOUS SOLUTION OF THE SODIUM PHENOLATE

Phenol	Percentage Extracted
Phenol.....	7.5
<i>o</i> -Cresol.....	20.8
<i>m</i> -Cresol.....	15.
<i>p</i> -Cresol.....	13.3
<i>o</i> -Ethylphenol.....	44.7
<i>p</i> -Ethylphenol.....	25.3
Dimethyl-2, 4-phenol.....	43.
Dimethyl-2, 5-phenol.....	37.7
<i>o</i> -Propylphenol.....	68.5
<i>p</i> -Propylphenol.....	28.7
<i>o</i> -Allylphenol.....	48.
<i>p</i> -Allylphenol.....	24.3
<i>o</i> -Isopropylphenol.....	72.7
<i>p</i> -Isopropylphenol.....	32.6
<i>o</i> -Butylphenol.....	80.7
<i>p</i> -Butylphenol.....	28.7
<i>o</i> -Pseudobutylphenol.....	97.
<i>p</i> -Pseudobutylphenol.....	30.6
<i>o</i> -Allyl- <i>o</i> -cresol.....	70.6
Di- <i>o</i> -propylphenol.....	97.7
Di- <i>o</i> -allylphenol.....	91.7
Thymol.....	88.
Carvacrol.....	82.5
<i>o</i> -Phenylphenol.....	52.5
α -Naphthol.....	14.7
β -Naphthol.....	23.

per cent of the amine had been extracted. After six extractions with ether, 76.32 per cent of the theoretical amount of oleic acid was removed. With more dilute solutions of the soaps slightly higher amounts of oleic acid were separated.

170. Extractions may also be made from an *organic medium by another organic solvent*, provided the two solvents are relatively insoluble in each other. Ligroin and aqueous methanol, ethanol, acetone, or acetic acid are suitable for this purpose. An excellent example is found in the separation of β -carotene and leaf xanthophyll.³ A mixture of 9.2 mg. of the former and 4.9 mg. of the latter was dissolved in 400 ml. of ligroin. It was then extracted six times with 300-ml. portions of 92 per cent methanol, the last extraction being colorless. In the ligroin there remained

9.75 mg. of material which was found by analysis to consist of 9.22 mg. of β -carotene and a small amount of xanthophyll which had not been extracted. This method of extracting a ligroin solution with 89 to 92 per cent methanol (95 per cent methanol extracts the β -carotene as well as the xanthophyll) has been used for the quantitative determination of these compounds in leaf tissue and was first employed by Willstätter and Stoll.⁴

171. Analysis by Extraction.—Extraction of acids from water solution by acid-free ether has been made the basis for determination of fatty acids⁶ in a manner reminiscent of their analysis by steam distillation (Duclaux numbers). Partition coefficients between ether⁶ and water of a series of acids are first determined. For instance, those of acetic, propionic, and butyric acids at 25° are 0.582, 0.272, and 0.103, respectively. Titrations of a sample of aqueous solution before and after extraction are made. The aqueous solution is brought to a definite normality (0.03 *N*) by addition of water or acid, and an aliquot portion (60 ml.) is extracted with a definite amount, *e.g.*, 100 ml., of ether. A portion (50 ml.) of the aqueous layer is then titrated from which the total amount of acid remaining in the water can be calculated.

172. Similarity of Extraction and Distillation Processes.—Processes of extraction are in some respects akin to those of distillation. In the latter case, two components are separated by fractionation, each plate growing progressively richer in one component, on a volatility basis. Likewise, in multiple extraction of a solution of two substances there will be a progressive separation determined by relative solubilities. The process is represented diagrammatically⁷ in Fig. 95, in which a mixture of *A* and *B* in solution in a solvent *E* is extracted with solvent *S*. Fresh portions of *E* and *S* are added to the products of the initial treatment as indicated in the diagram. By combinations and extractions the combined solutions *S* eventually become richer in component *B*, and those of solution *E* become correspondingly richer in *A*. Hunter and Nash calculate the efficacy of this method of fractional distribution: Suppose that the mixture contains 100 g. each of *A* and *B*, that it is treated at all stages with equal volumes of the two immiscible solvents *S* and *E*, and that the distributions of *A* and *B* in each solvent are represented by equations

$$K_A = \frac{C_S}{C_E} = 0.25$$

$$K_B = \frac{C_S}{C_E} = 4.00$$

where K_A and K_B are the respective distribution coefficients and C_S and C_E are the appropriate concentrations of A and B . For

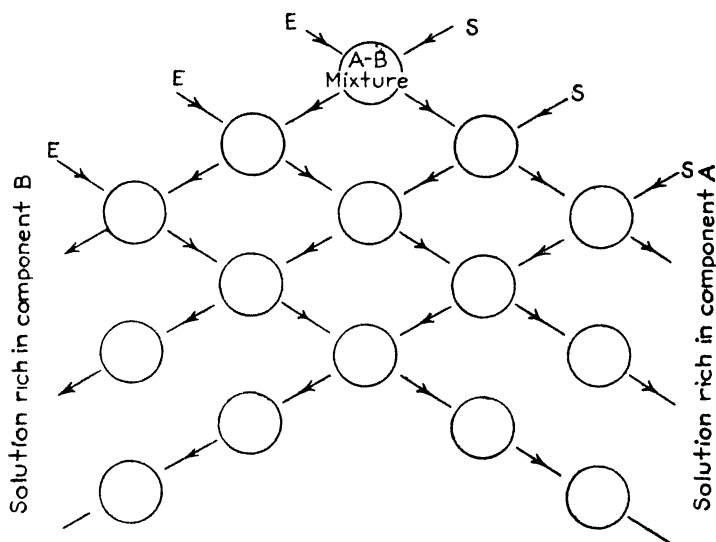


FIG. 95.—Multiple fractional extraction.

the three fractions of each solvent as indicated in the diagram, the enrichments will be as shown in Table 65. The total loss of

TABLE 65.—CALCULATED ENRICHMENT IN EXTRACTION PROCESS

Fraction	G. solute in fraction	Percentage by weight of B in separated solute	Fraction	G. solute in fraction	Percentage by weight of A in separated solute
S_1	51.5	99.0	E_1	51.5	99.0
S_2	25.4	98.5	E_2	25.4	98.5
S_3	12.2	98.4	E_3	12.2	98.4
Total.....	89.1	98.8	Total	89.1	98.8

material amounts to 11.9 g. out of the original 200, and *A* and *B* are obtained in 98.8 per cent purity. This rapid separation is possible only when there is a considerable difference in the distribution ratios of the two substances in question. If the values are nearer to each other than those used in the illustration, a separation equivalent to the foregoing would require many more extractions. Thus, if K_A and K_B were 0.33 and 3.00, respectively, six additions of fresh extracting solvent *E* and *S* would have to be made to obtain the same enrichment as is given by three additions in the example quoted.

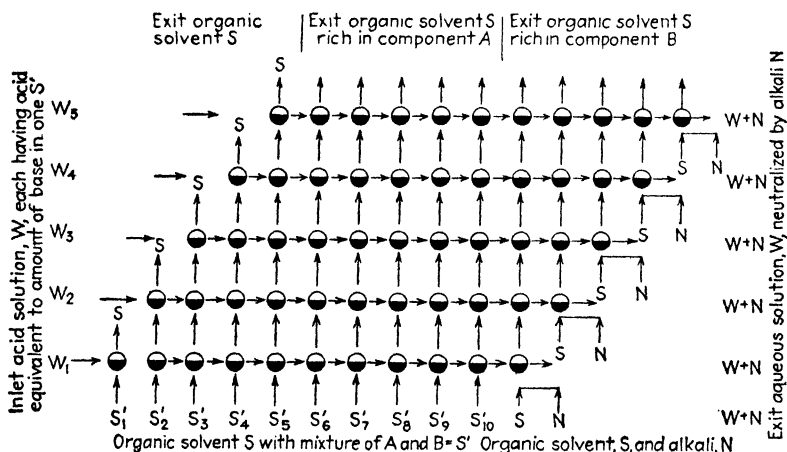


FIG. 96.—Multiple-fractional-extraction method for separation of two bases.

Of great interest to the organic chemist is the *separation of isomeric organic bases* from hydrochloric acid solution by multiple extraction⁸ with an organic solvent such as ether or benzene. The complete diagram is given in Fig. 96, in which 10 solutions *S'* of equal volume, each containing the same amounts of the two bases to be separated, are treated with 5 aqueous solutions of hydrochloric acid, each containing acid equivalent to the amount of base in one of the solutions *S'*. The beginning of the process (lower left-hand corner) occurs when the first organic solution is extracted with the first acid, a step that should result in stripping the organic solvent of its base unless some hydrolysis occurs. The stripped solvent is discarded (exit organic solvent), and the aqueous extract (dark

semicircle) is shaken with the next solution S_2 . There will now be an exchange of bases between these two solutions depending on the relative dissociation coefficients of the components. Thus, if base B is stronger than A , it will combine with most of the acid,

Before shaking		After shaking	
In aqueous solvent	In organic solvent	In aqueous layer	In organic layer
$\left. \begin{array}{c} B \\ H \\ Cl \end{array} \right\} + \left. \begin{array}{c} A \\ H \\ Cl \end{array} \right\}$	$+ \left\{ \begin{array}{c} B \\ + \\ A \end{array} \right.$	$\left. \begin{array}{c} B \\ H \\ Cl \end{array} \right\} + \left. \begin{array}{c} A \\ H \\ Cl \end{array} \right\}$	$\left\{ \begin{array}{c} A \\ + \\ B \end{array} \right.$

FIG. 97.—Distribution of two bases of different strength, A and B , in aqueous and organic layer.

forcing the larger quantity of A into the organic solvent. The change can be represented in the form of an equation (see Fig. 97) in which the proportion of bases in the aqueous and organic phases after shaking is illustrated by the relative size of the type.

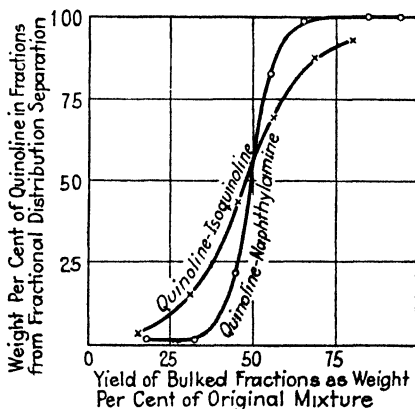


FIG. 98.—Systematic separation of bases by extraction of benzene solution by aqueous solutions of the hydrochloride salts.

The organic layer is then treated with the next acid extract W_2 , and the aqueous layer is shaken with solutions S_3 , etc. The extractions are continued until all of the original solutions have been treated in this manner with the aqueous extracting

solution. The acid portion at the completion of each series is neutralized (*N*) and extracted with fresh solvent in order to make contact with the next series. The success of the method may be judged from Fig. 98, which shows that substantially complete separation was possible with equimolecular mixture of α -naphthylamine and quinoline and partial separation with isoquinoline and quinoline. Just as more complete fractionation is possible with distillation columns by increasing the number

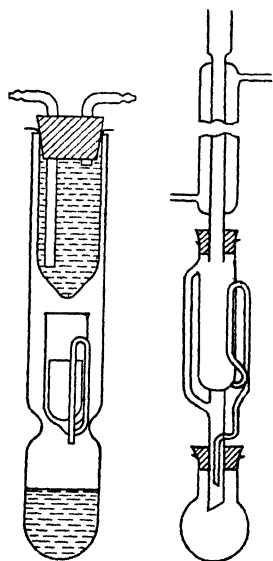


FIG. 99.—
Wasitzky's ap-
paratus for ex-
traction of
micro quanti-
ties of material.

FIG. 100.—
Soxhlet ex-
traction ap-
paratus with-
out thimble.

of plates and the reflux ratio, so does the process of fractionation by extraction find a parallel improvement in increasing the number of portions of the organic solution *S* and in employing more acid portions *W*. In actual practice this extraction is not difficult or cumbersome to carry out. The number of containers is not excessive if stock solutions of *S'* and *W* are made up and aliquot portions withdrawn as needed.

173. Apparatus for Continuous Extraction of Solids.—Wasitzky⁹ has described an apparatus for *micro* work which is made from two test tubes (see Fig. 99). The outer tube is 20 cm. long, and the siphon cup is 50 mm. long by 12 mm. wide. A test-tube condenser is set loosely in the top of the outer tube. The material is contained in a filter-paper cup. He claims that the results are as accurate for 1.2 g. in this

micro apparatus as they are for 25 g. on a macro scale.

Extractors of the *Soxhlet* type work on the principle of complete immersion of solid in the liquid with periodic siphoning off of solvent and replacement by fresh liquid. The manner of operation is made clear by reference to Fig. 100 in which vapors from the boiling flask are condensed so that the liquid falls into the siphon cup from which it is returned periodically to the flask. Larger capacity extractors can be constructed readily on this

same principle. The apparatus of Drake and Spies¹⁰ is illustrated in Fig. 101. This apparatus was designed to take a charge of 10 lb. of ground roots and seeds. It was constructed from a 12-l. short-necked flask in the bottom of which was sealed a 3-in. (7.5-cm.) length of 25-mm. tubing which ended in a short piece of 5-mm. tubing by which a connection of rubber tubing over the glass-to-glass contact could be made to the siphon tube. On the bottom of the flask and covering the outlet tube was a large thin cork pierced with several holes, which supported a breather tube. On top of the cork was a layer of cotton on which material to be extracted rested. The breather tube permits clean siphoning by eliminating resistance of the mass to passage of air. A 12-l. three-necked flask served as the boiler, and a steam-heated copper spiral in the center opening furnished heat. The upright condenser is of a type used by Cameron¹¹ because it is nonflooding. With methanol as the solvent, siphoning occurred every 45 min. The apparatus is free from all ordinary fire hazards. Schulz¹² has made a large Soxhlet extractor from tin cans to which is soldered copper tubing to complete the usual assembly. The lid is made tight by cement. The apparatus shown in Fig. 108 can also be used for extraction of solids provided a loose cotton plug is placed in the bottom or the material is put in a cloth bag.

174. Commercial *thimbles* made of fiber or alundum are used as containers in small extractors. In the case of large apparatus the material is frequently put in a cloth bag of suitable dimension. Williams¹³ prepared his own thimbles of the desired size and permeability by mixing stoneware clay (obtained from a manufacturer of stoneware) with an equal weight of anthracite coal,

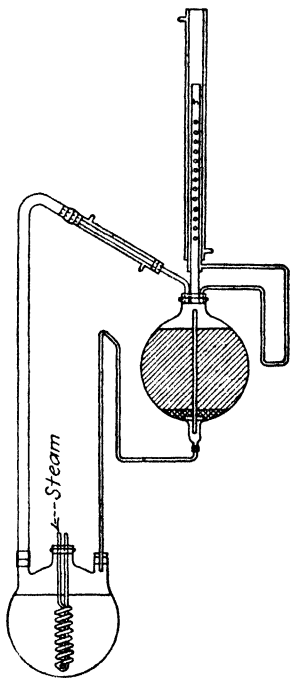


FIG. 101.—Apparatus of Drake and Spies for extraction of large quantities of material.

molding, and firing the mixture to 1050°C. according to carefully prescribed directions.

175. Many *extractors without siphons* for solids have been used. The simplest of these is the ordinary coffee percolator. Haller and LaForge¹⁴ extracted 2 kg. of ground Derris root repeatedly in a percolator at ordinary temperatures with petroleum ether (b.p. 30 to 60°). It required about 20 l. of solvent to exhaust the material. Clarke¹⁵ used a funnel with the material in a fluted filter paper and a round-bottom flask set on top as a condenser (see Fig. 102). It was satisfactory with quantities up to 500 g. and permitted little loss of solvent even with ether. Tanner¹⁶ employed a tall beaker in which a distilling flask could be placed (see Fig. 103). The condensate dropped upon the sample wrapped in a filter paper and supported on a glass triangle above the boiling solvent. A siphon cup may also be used. Claim is made that it operates faster than the funnel type and avoids choking of ascending vapors with condensate. Another

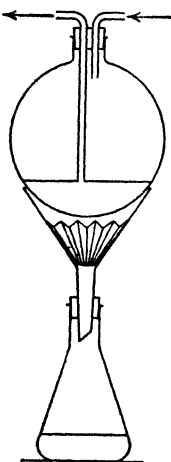


FIG. 102.—Extraction apparatus made from an ordinary funnel.

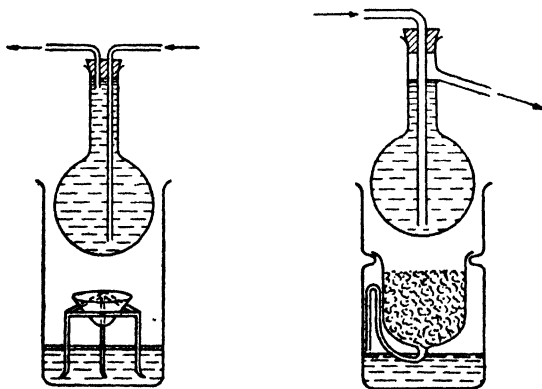


FIG. 103.—Extraction in beakers.

extractor,¹⁷ useful also with liquids, is pictured in Fig. 104. Kuhlmann¹⁸ suspended a bag in or below a condenser.

176. An *upward-displacement extractor* has been employed by Holmes.¹⁹ The special advantage claimed in this type is that there is no channeling. A simple form of his apparatus is illustrated in Fig. 105. The outer tube is 55 mm. long by 26 mm. in diameter. An inner tube of a size to give about 2 mm. clearance rests on a plug of cotton or a layer of ignited sand at the bottom. Glass guides keep the inner tube in position. The sloping condenser directs the condensate to the wall where it flows down through the annular space, up through the solid material being extracted, and down through the center tube which should be

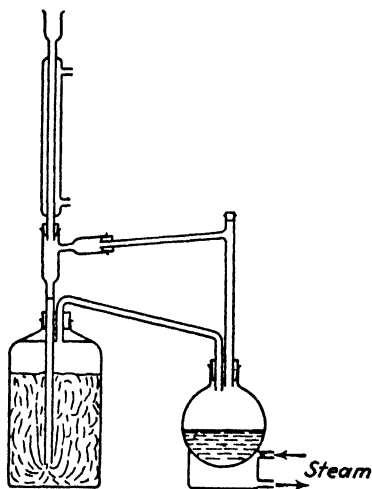


FIG. 104.—Continuous extraction in a large bottle.

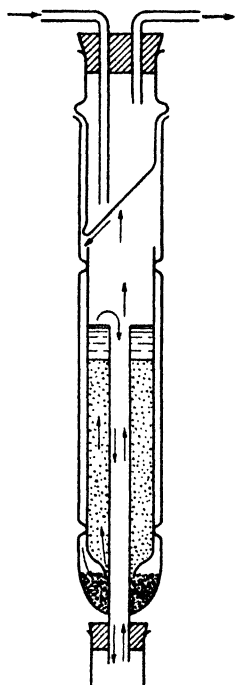


FIG. 105.—Upward-displacement extractor to avoid channeling.

at least 10 mm. in diameter in order to avoid any obstruction of upward-moving vapors by return liquid. A cotton plug may be inserted above the solid in the inner tube to prevent material from floating to the top from where it might be carried into the flask. This return tube must, of course, be closed by a cork or a wire during loading. The apparatus was used by Holmes in extraction of cottonseed meal where channeling was bad.

177. Choice of *solvents for continuous* extractions is often of as much importance as in single extractions. Thus, wet ether was found to be a far better solvent than ordinary ether in extraction of gossypol²⁰ from cottonseed meal (0.0424 as compared with 0.0193 per cent). Only 5 ml. of water to 350 ml. of ether is necessary to effect this change. Continuous extraction of organic acids from tobacco leaf²¹ is practically quantitative if the material is first acidified to approximately pH 1 by sulfuric acid. Stepwise extraction is very convenient as a method of separation of some constituents. When cottonseed meal²⁰

was first extracted with petroleum ether—a process that removed part of the oil—the subsequent extraction with ethyl ether yielded a product containing purer gossypol than if the first step had been omitted.

178. **Continuous Liquid-liquid Extractions** may be divided into two classes depending on the relative specific gravity of the liquids involved. For *extractions with lighter liquids* the previously described apparatus (Fig. 104) constructed from a bottle can be used. Marshall²² has employed a large distilling flask after the manner shown in Fig. 106.

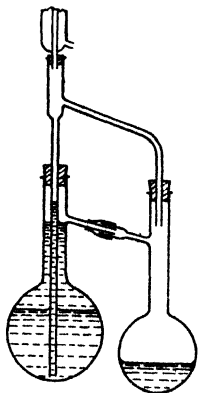


FIG. 106.—Continuous extractor made from two flasks.

These pieces of apparatus require connection at two points which is not usually so convenient as a single adjustment. A construction shown in Fig. 107, has a minimum number of projecting parts which can be broken, is simple to construct, and very effective. It has been used by a number of investigators.²³

For *extractions with heavier liquids* apparatus of the type shown in Fig. 108 is very convenient. The method of operation is obvious after a little study. Mays and Warren²⁴ have designed units that can be attached to any flask, condenser, and bottle. Figure 109a shows the arrangement for extraction of a solid or of one liquid by another heavier one (the loop is essential to promote siphoning in wide tubes); and Fig. 109b, for extraction with a lighter liquid. In either case the flask containing the extracting solvent is attached at *S*, the condenser at *C*, and the neck of the bottle or other container at *E*.

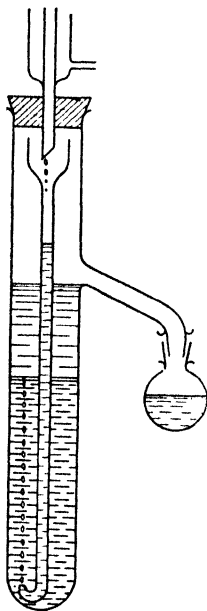


FIG. 107.—Extractor with single connection to flask for extracting a heavier liquid with a lighter one.

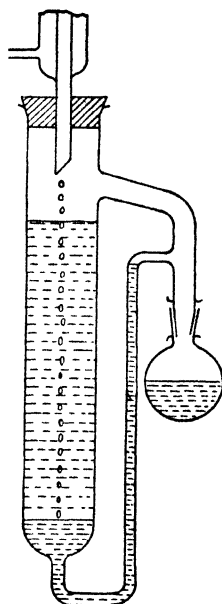


FIG. 108.—Apparatus with single connection to flask for continuous extraction of a liquid with a heavier

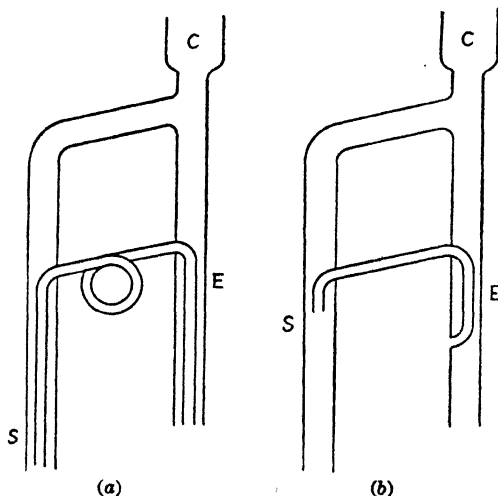


FIG. 109.—Continuous-extraction apparatus of Mays and Warren for attachment to ordinary flasks; (a) for solids, (b) for liquids heavier than the extracting liquid.

179. Continuous *air-lift extractors* depend upon a current of air to lift the extracting liquid* to the head of the column whence it can flow by gravity through the solid or liquid being extracted. Such a device was employed by Moore²⁵ (see Fig. 110). Chapman and Hammett²⁶ also used the same principle to circulate carbon tetrachloride through an aqueous solution containing benzoic acid. Recovery of the extracted acid was made by allowing the tetrachloride to fall through caustic solution before being recirculated. Loss of extracting solvent was avoided by bubbling the air through carbon tetrachloride before entering the system.

FIG. 110.—
An air-lift ex-
tractor.

180. Continuous *countercurrent liquid-liquid* extraction systems have been employed. Leslie²⁷ separated the aromatic compounds from gasoline by extraction with sulfur dioxide. Varteressian and Fenske²⁸ have also studied the performance in a column packed with rings of the same type used in fractional distillation.

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* Another useful application of the air lift should be mentioned. Replacement of the extracting chamber by a condenser permits circulation of either cold or warm liquids through the jacket. Usually the elevated liquid is discharged into a reservoir kept at the desired temperature whence it flows by gravity through the condenser and back to the air lift.

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CHAPTER XI

SPECIAL METHODS AND APPARATUS

MICROMANIPULATION

181. All operations commonly carried out *with solid substances* in a beaker can be performed as well in capillary tubes 2 to 3 mm. in diameter with quantities as small as 2 to 3 mg. The procedure is very simple and, with a little practice, becomes a quick and efficient method of carrying out a reaction and purifying the product. *Apparatus*, which is easy to construct, consists of:

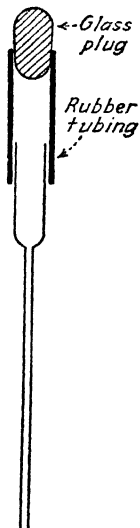


Fig. 111.—
Capillary pi-
pette for micro
work.

1. Capillary tubes approximately 2 mm. in diameter made by drawing glass tubing to required size and sealing one end.

2. A capillary pipette, which fits easily into the capillary reaction tubes mentioned above, constructed by drawing out the end of a medicine dropper or by attaching a short section of rubber tubing, closed by a glass plug at one end, to glass tubing from which the capillary is constructed (see Fig. 111).

3. Capillary stirring rods which are made by drawing out ordinary glass rods to dimensions small enough to fit into the capillary tubes.

4. A small hand-operated centrifuge.

5. Baths, made either by boring appropriately sized holes in metal (brass is satisfactory) blocks or by using a beaker containing oil, in which the tubes can be heated, if necessary, in a horizontal position.

Weighing can be done on an analytical balance, the time factor being reduced to a reasonable amount by magnetic or air damping. Simple balances may also be constructed from quartz fibers (see Fig. 112), one end being firmly fixed, and the other holding a light metal pan or other support and moving in a calibrated arc. Volumes of liquids can be estimated by calibrating the pipette or by calculating

the volume per millimeter height from the diameter of the capillary tube.

The *general procedure* is to put measured quantities of reagents in the capillary reaction tube and centrifuge in order to force the contents to the closed end. The open end is sealed, and the tube heated to the temperature desired. When reaction is over, the tube is cooled, centrifuged if necessary, and opened. If crystals are present, they are broken from the glass by the capillary stirring rod and centrifuged to throw them to the bottom. The mother liquor is then taken off with the capillary pipette. The crystals may be washed and stirred with the capillary rod, centrifuging and removing the mother liquor as before.

Drying is accomplished by putting the tube in a block or other container which can be heated at a temperature below the melting point of the compound. A current of dry air is directed over the surface of the solid through a capillary tube (see Sec. 23).

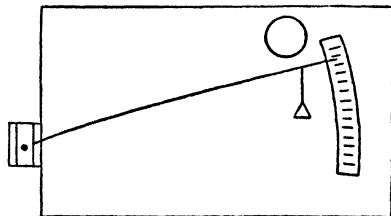


FIG. 112.—Quartz-fiber balance.

The *melting point* can be determined in the tube by merely inserting it in any conventional melting-point apparatus. The greatest error arises from inadequate drying of the sample. *Digestion* and *recrystallization* can be performed by adding an appropriate liquid, sealing if necessary, heating, and recovering the crystals as described before. As many as 10 to 12 recrystallizations with melting-point determinations after each one can be made with these small quantities of material.

Filtrations on a micro scale have already been described in Sec. 139. Where hot or cold filtration is necessary, the centrifuge tube holder can be filled with a liquid at the desired temperature, and the capillary reagent tube centrifuged as before. Decolorizations with carbon can similarly be effected.

Sublimations are easily carried out by inserting the end containing the sample in a metal block or by holding it a little distance above a micro flame and wrapping a piece of wet filter around the capillary tube where collection of sublimate is desired.

Sublimations under vacuum are made similarly, except that a section of tubing from which the capillary is constructed is left attached for convenience in connecting to the pump. After sublimation the lower end of the capillary is broken off, the open end sealed, the crystals broken loose from the glass with a stirring rod, the tube centrifuged, and the melting point observed. (For other methods of micro sublimation see Sec. 184.)

The usual methods of *crystallizing* suffice in these small tubes. Thus, the solvent may be allowed to evaporate slowly by placing the tube in a warm closet overnight or may be removed rapidly by a current of cold or warm air injected into the tube through another capillary or may be diluted with a precipitating liquid. Solutions may be chilled by immersing tubes in freezing mixtures. A piece of filter paper, wet with ether or other low-boiling solvent and wrapped about the tube adjacent to the sample, enables freezing temperatures to be attained from rapid evaporation of the solvent. As an example of the possibilities in separating mixtures of substances by crystallization, reference can be made to Fuchs's¹ recrystallization of 4 mg. of a mixture of hydroquinone with 40 per cent resorcin from hot water six times. The melting points beginning with the original sample were 143, 158, 163, 165, 166, 166.5, 168°C. The total time for the purification was 3.5 hr.

182. Experiments devised by Fuchs and described below illustrate the wide variety of reactions that can be performed on a micro scale. In fact there is scarcely any reaction that cannot be handled with these small quantities. It is also true that the same technique can often be used to advantage in 4-mm. tubes with 10 to 20 mg. of material.

m-Dinitrobenzene from Nitrobenzene.—Heat 2 mg. of nitrobenzene in a tube with 5 mg. of a mixture of 2 parts concentrated sulfuric acid: 1 part fuming nitric acid in a closed tube for two or three minutes at 180°C. Cool, open the tube, add water, wash well, and dry. The product can be recrystallized from hot alcohol and washed with cold alcohol until a constant melting point is reached (m.p. 90.5°C.).

Thiocarbanilide.—Heat 2 mg. of anilin with an equal volume of alcohol and carbon disulfide for 2 hr. in a closed tube at 100°C. Cool; open the tube; and wash with water, with dilute hydrochloric acid, again with water; and then dry. The product can be recrystallized from hot alcohol (m.p. 152°C.).

Benzenesulfonamide.—Stir 3 mg. of benzenesulfonyl chloride with 3 mg. of ammonium carbonate at 100°C. Centrifuge as necessary to keep the mixture in the bottom of the tube. The reaction is over in 15 min. Wash with water and dry. The product is soluble in hot alcohol and is recrystallized by addition of hot water (m.p. 153°C.).

Acetanilide.—Heat 3 mg. of acetic acid with 2 mg. of aniline in a closed tube for $\frac{1}{2}$ hr. at 150°C. After opening the tube, add water and recrystallize from hot water (m.p. 114°C.).

m-Bromobenzoic Acid.—Heat 8 mg. of benzoic acid with the corresponding quantity of bromine in water for 6 hr. at 160°C. The product is dissolved in alkali and precipitated by hydrochloric acid. It can be recrystallized from hot water (m.p. 154°C.).

Benzoin.—Heat 3 mg. of benzaldehyde with twice the amount of 50 per cent alcohol and 0.3 mg. of potassium cyanide in a closed tube for 20 min. at 150°C. Wash the crystals with alcohol. Recrystallize from hot alcohol (m.p. 136°C.).

Benzil.—Heat 2 mg. of benzoin with twice the quantity of nitric acid (1.41) in a closed tube at 100°C. for 1 hr. The crystals are precipitated by the addition of water. Wash with cold and recrystallize with hot alcohol (m.p. 95°C.).

Benzilic Acid.—Mix benzil with an equal quantity of solid caustic alkali and water. Heat in a closed tube for 10 min. at 100°C. Open and cool to low temperatures to precipitate the salt. Remove the mother liquor. Dissolve the crystals in hot water and precipitate by addition of dilute hydrochloric acid. Wash with water until free from acid; dry; and recrystallize from hot water (m.p. 150°C.).

Cinnamic Acid.—Heat 4 mg. of benzaldehyde with 6 mg. of acetic anhydride and some sodium acetate at 180°C. for 2 hr. Wash the reaction mixture with water and recrystallize from hot water. Dry. Recrystallize from ligroin and from hot water (m.p. 133°C.).

Anthraquinone.—Heat 4 mg. of anthracene with acetic and chromic acids for 15 min. at 150°C. Wash the product with water, alkali, and again with water (m.p. 271°C.). *Danger!* Pressure is developed in this tube. Goggles must be worn, and the tube handled in a handkerchief or small towel when removed from the metal block.

Hippuric Acid.—Heat 2 mg. of glycine with 3 mg. of benzoic anhydride until the appearance of a red color. Dissolve in hot water, add decolorizing carbon, and filter. Wash with alcohol and petroleum ether. Recrystallize from hot water and wash as before (m.p. 186°C.).

Benzoic Acid from Benzonitrile.—Heat benzonitrile with sulfuric acid (1:3) for 5 min. at 210°C. Wash with water and recrystallize from hot water (m.p. 121°C.).

Naphthalene Picrate.—Add 3 mg. of naphthalene in alcoholic solution to an excess of a warm saturated alcoholic solution of picric acid. On cooling, yellow needles are formed. Wash with 50 per cent alcohol (m.p. 149°C.).

Zinc-dust Distillation.—Draw a pyrex tube of about 5 mm. inside diameter, down to usual capillary dimensions at one end (see Fig. 113). Constrict

the tube at *a* and insert a plug of ignited asbestos at *b*. Add a 2.5-cm. layer of zinc dust and then a 0.5-cm. layer of zinc dust and 5 mg. of substance. Seal the tube at *a*. Heat with a micro flame, beginning with the end containing pure zinc dust. Anthracene sublimes into the open capillary tube. If heating is too rapid, anthraquinone is driven through unchanged. The capillary tube is next cut off, one end sealed, and the product treated to the usual centrifuging, purifying, and determining of melting point.



FIG. 113.—Tube for micro zinc-dust distillation.

183. *Micromanipulation with liquids* has already been described in some detail in Sec. 54 and 69 on micro boiling points and microdistillations.

SUBLIMATION

184. When a compound in the solid state has a relatively high vapor pressure, it is often possible to volatilize without melting it. This process of distillation of solids without melting is termed sublimation. On a *micro scale* the apparatus of Soltys² (Fig. 114) is very satisfactory. The sample (5 to 30 mg.) rests on a porous sintered-glass plate sealed into a tube 14 cm. by 12 mm. in diameter. An upper layer of ignited asbestos keeps it in place. The position of the gas inlet must be adjusted to avoid dislodging or backward sublimation. A metal block is the source of heat.

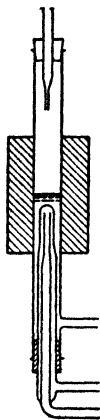


FIG. 114.—
Microsublimation
apparatus of
Soltys.

Temperatures of sublimation may be observed in the microscope melting-point apparatus of Kofler and Hilbeck (see Sec. 47). Brown,³ using the method of Eder and Haas,⁴ observed sublimation points under vacuum of a number of amino acids. The sublimate was collected on a microscope cover glass which was seated in the path of the vapors. The cover glass could then be transferred to a micro melting-point apparatus, and the melting point determined without any handling of crystals. Under carefully regulated conditions, sublimation temperatures were reproducible. These values, together with the melting point, served as a test for

purity. Kempf⁵ was able to detect 0.000000001 g. of indigo by a micro-vacuum sublimation.

Microsublimation in a capillary tube was carried out by Benedetti-Pichler⁶ with the apparatus shown in Fig. 115. The material to be sublimed is first put into the capillary and centrifuged in order to throw it to the bottom. The aluminum

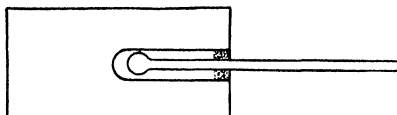


FIG. 115.—Microsublimation apparatus.

block is provided with a hole for a thermometer. Other operations are obvious.

185. *Sublimation on a larger scale* may conveniently be done in a beaker in which a flask is set as a condenser. Robinson and Deakers⁷ describe an apparatus (see Fig. 116) for the sublimation of anthracene which is very useful. The same authors

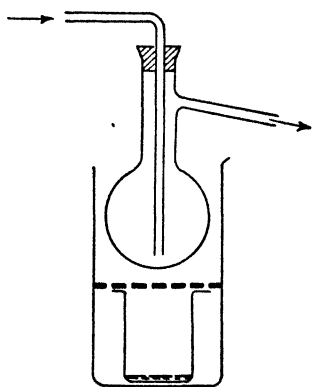


FIG. 116.—Apparatus for sublimation in a beaker.

collected naphthalene and benzoic acid, distilled from a retort into a flour or sugar bag through which cold air was also blown to aid in condensing the material. Dony⁸ found that shape and orientation of crystals were governed by convection currents. As an apparatus, he used glass accumu-

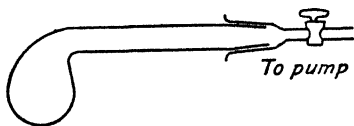


FIG. 117.—Apparatus of Kempf for vacuum sublimations.

lator jars in which graphite cupels containing nichrome heaters were suspended as vapor generators.

183. Vacuum-sublimation apparatus for larger quantities of material may be of the tube variety similar to that shown in Fig. 114, for micro work. It is also possible to suspend a platform carrying a heating element in a vacuum desiccator, using an inside condenser for any necessary cooling. The arrangement

of Carothers and Hill,⁹ consisting of two vacuum desiccator tops (see Fig. 65), is very convenient, for it allows connections to be brought in from both top and bottom. Their assembly was designed for a molecular still, but the apparatus is applicable to sublimation processes under a vacuum. The apparatus used by Kempf¹⁰ in his voluminous work on sublimation is shown in Fig. 117.

AGITATION

187. Stirrers.—Stirring apparatus is necessary for a large number of operations in the laboratory. An electric motor may be used as the source of power, but the initial cost and the need of frequent repair often make such units a luxury. If compressed air is available, it is possible to satisfy most of the requirements by a simple air turbine made by cementing metal vanes into a number of slits cut deep into the circumference of a one-hole rubber stopper which, in turn, is slid on to the shaft of the stirrer. The shaft is supported in commercial ball-bearing assemblies after the manner suggested by Hershberg,¹¹ who fitted a short section of pressure tubing into the center of a ball-bearing assembly so that the rod could be held firmly (see also Sec. 37).

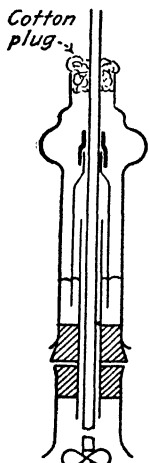


FIG. 118.—
A mercury-sealed stirrer.

Propeller blades are usually most serviceable as stirrers. For special purposes, glass or metal chains¹² can be hung on a ring so that they will pass through the neck of a flask but spread when the stirrer is in motion. Stirrers which draw the liquid through an opening in the bottom and spray it out near the surface are often used. Patterson¹³ gives exact specifications for both upflow and downflow stirrers of this type. Stirrers that operate at 10,000 r.p.m. or more have a pronounced effect in many reactions.¹⁴ Square-shaped containers are usually better than round ones.

Where an apparatus is too small to admit a stirrer, adequate agitation is possible by allowing the hammer of an electric bell to vibrate against the container, loosely supported at the top.

Mercury-sealed stirrers¹⁵ are necessary where air or moisture must be excluded, gases collected, or solutions refluxed. Their construction is illustrated in Fig. 118. The parts may be made of iron as well as of glass, although the latter has the advantage of visibility. Another sealed stirrer, suitable for many purposes, is shown in Fig. 119.

188. Shaking machines are usually available commercially. Simple constructions from door springs and other parts have been described by Bent¹⁶ and by Morton.¹⁷ These pieces of apparatus are easy to operate because they have a natural period of vibration. Weir, Houghton, and Majewski,¹⁸ and Highberger¹⁹ have also described mechanical assemblies which are easy to construct.

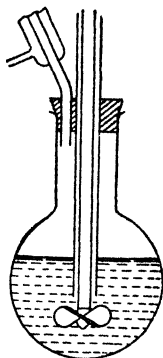


FIG. 119.—Method of sealing stirrer with a liquid.

REACTIONS IN AN INERT ATMOSPHERE

189. It is often necessary to carry out filtrations and other processes in a sealed apparatus for which the ordinary mercury-sealed stirrer is not adequate.

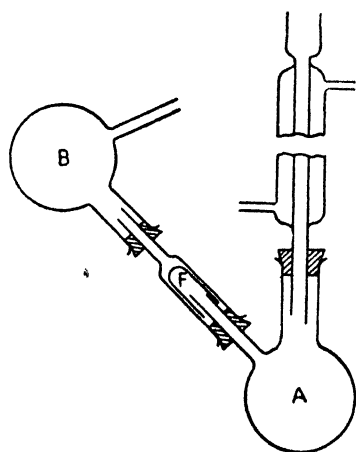


FIG. 120.—Schmidlin's apparatus for carrying out a reaction in an inert atmosphere.

Schmidlin's²⁰ apparatus (see Fig. 120) is a common type used for such purposes. Inert gas, preferably saturated with vapors of the solvent, can be passed into flask B, through the adaptor and filter F, and into the reaction flask A, whence it escapes through the condenser. When the reaction is over, the direction of gas flow is reversed, the apparatus is pivoted on a single rod support, and the contents are filtered through the filter thimble from A to B. Flask A may then be cleaned and used

in like manner if desired in the filtration of the product in B. Other methods of using the apparatus are obvious.

Ziegler²¹ describes an apparatus that is very useful. It consists (Fig. 121) of two tubes connected by a bridge which has an asbestos or cotton filter. In the preparation of a free radical, dried silver powder and the triarylchloromethane are put in one arm A, and solvent into the other B, after which the

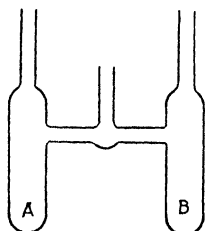


FIG. 121.—Ziegler and Schnell's apparatus for carrying out reactions in a vacuum atmosphere.

apparatus is evacuated and sealed. The solvent is then distilled from B to A by cooling the latter. After reaction is completed, the solution is filtered into B and concentrated by distilling the solvent into A. Upon crystallization, the mother liquor is filtered into B, and the arm A is sealed and detached.

The Schlenk²² tube is shown in Fig. 122 attached to another unit ready for a filtration. In some cases a flask may be stoppered and shaken in a machine with no necessity for an all-glass seal. Thus, Bachmann and Wiselogle²³ prepared triphenylmethylsodium from the triaryl-methylchloride and sodium by shaking the ether solution with some broken glass in a stoppered container.

Where a solid phase must be removed or filtered from a reaction mixture it is possible sometimes to use an apparatus similar to a tea ball.²⁴ A free radical, for example, can be prepared by suspending a bag of metallic silver in a boiling solution of the chloride in a solvent and withdrawing the bag when reaction is complete. The column of vapor, which can be made as high above the boiling solution as desired, insulates the mixture against air.

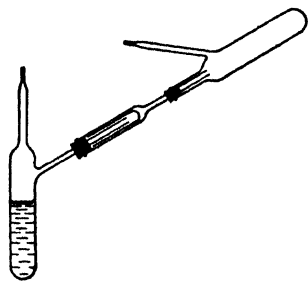


FIG. 122.—Schlenk tubes for use with reactions affected by air.

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EXPERIMENTS

(Note. Study the discussion in the text before performing any experiment.)

MICROMANIPULATION

Micropreparations are given in Sec. 181; micromelting points, in Sec. 46.

Experiment 1. *Microboiling Points.*—Determine the boiling point of a drop of benzene and of toluene by the Emich and the Siwoloboff methods (see Sec. 54). The observed should agree with the correct values within 0.5° . Possible errors with the Emich methods may arise from inadequate stirring of the bath or from entrapping too much air when sealing the tube. Tapering the end of the capillary tube to hairlike dimensions will ensure that the entrapped air bubble is not too large.

Experiment 2. *Microfractionation.*—Into an Emich fractionating tube (Sec. 69) weigh 20 to 25 mg. of a mixture of 2 volumes of benzene to 1 of xylene. Centrifuge to effect intimate contact of liquid with asbestos. For convenience in recording results make about 20 Emich boiling-point tubes and insert them in a sheet of paper or in holes bored in a large cork stopper. Put the fractionating tube, jacketed and in a vertical position, in a copper block and begin heating. Raise the temperature very slowly when in the vicinity of the boiling point. If the rise has been too rapid, remove the tube, centrifuge, and repeat the operation. As a matter of fact, better results are obtained by heating and centrifuging about three times before collecting any sample. When the first tiny drop passes the constriction, remove it by inserting capillary tube 1, which is then sealed and restored to its numbered position until its boiling point can be determined. Remove the fractionating tube from the block, centrifuge to throw down the portion of the drop not removed, and repeat the operation, using the second capillary tube. Continue in this manner until all of the liquid has been

distilled. Determine the boiling point of each fraction by the Emich method. Plot boiling points versus fraction number. The total time, 3.5 to 6 hr., varies with the accuracy desired.

Even better fractionation may be carried out using a capillary tube approximately 2 mm. in diameter packed with glass wool for a length of about 11 cm. Make the usual constriction in the tube just above the packed section. Insert the drop to be fractionated, centrifuge to throw it to the bottom of the tube, and set the latter, jacketed with asbestos, in the block. Heat until the first droplet collects above the constriction. Centrifuge and repeat the operation. Then begin collecting the droplets in the boiling-point tubes which have previously been prepared. As before, there will be approximately one boiling-point tube needed for every milligram of liquid in the sample. A single drop, 25 to 35 mg., containing equal parts of benzene and toluene, can thus be separated if distillation is very slow. Assuming that the weight of each part is very nearly the same, construct a curve showing percentage composition versus boiling point.

Experiment 3. *Microsublimations or Distillation under Vacuum.*—Draw out the end of a 7- to 8-mm. tubing to capillary, *i.e.*, 2-mm. dimensions. Seal the capillary at the desired length (about 5 to 7 cm.) and cut off the larger end until only enough to make a satisfactory connection to the pump remains. Introduce 2 to 3 mg. of the material to be sublimed or distilled and centrifuge to throw it to the bottom of the capillary. Sticky or gummy material may be handled by scraping it into a smaller capillary, wiping the outside clean, and dropping the filled section into the larger one. Insert the capillary in a hole in the metal block, attach the pump (water, oil, or mercury diffusion pump), and wrap a piece of wet filter paper around the capillary at the place where condensation is desired. Heat the block until the material sublimates or distills. If oily or undesired liquid collects, drive it farther up the tube by shifting the position of the wet paper condenser. When sublimation is completed, stop the operation, cut off the lower end containing the residue and the upper larger end, seal the capillary, purify, and determine the melting point of the sublimate or condensate. Indigo is a very suitable material for sublimation under vacuum.

Similar operations can be carried out with liquids. The boiling point under reduced pressure can be determined by inserting an inverted capillary (Siwoloboff method) into the larger capillary distillation vessel. Sublimations at atmospheric pressures are made in micro tubes. Anthracene may be used as the compound to be sublimed.

SEPARATION AND PURIFICATION OF COMPOUNDS

Experiment 4. Fractionation.—Use a fractionating column, preferably one with at least 12 theoretical plates, which is insulated by a jacket whose temperature can be controlled. The following directions are designed for a total condensation-variable take-off column (see Sec. 79). Attach the flask, containing 20 ml. of a mixture of equal volumes of benzene and toluene, to the column. Adjust the jacket temperature to a point near to or identical with that of the compound being distilled. Begin the distillation, using a small flame under the flask. Keep the stopcock at the take-off closed until equilibrium conditions have been reached, *i.e.*, until the thermometer reads the lowest temperature possible while its bulb is wet with condensate. When this point is reached, open the cock enough to allow drops to fall at a regular rate. Jacket and column temperature should theoretically be the same. Efficient fractionation is aided by an increase in reflux ratio which is varied by adjusting the stopcock. In changing to a higher boiling fraction, raise the reflux ratio. In fact the stopcock can be closed entirely until equilibrium is attained after which it is opened to drain a few drops and closed again. Repeat this process until the temperature becomes constant at the boiling point of the next fraction, after which the cock can be adjusted for collection at a regular rate. Do not allow the column to flood if efficient fractionation is desired. When a low-boiling component is exhausted, some flooding may occur before the jacket temperature is raised and the next fraction collected. At this point close the stopcock until proper conditions of jacket temperature and reflux have been reached. Slight cases of flooding can often be corrected by blowing on the distilling flask above the liquid level in order to condense enough vapor to drain the flooded section. Plot

milliliters of condensate versus temperature. Compare the result with that expected from the determination of the theoretical plate (Experiment 16). Twelve theoretical plates are required to make a complete separation of benzene from toluene.

If a partial-condensation stillhead is used on the column, adjust the circulating liquid in the dephlegmator until a suitable reflux ratio is established. Good ratios vary from 10 to 30 or an even higher number of drops of reflux to 1 of condensate. If the boiling point of the compound is above 100° , a current of air through the dephlegmator is sufficient.

Although flooding in the column during distillation reduces the effective area of the packing and thus diminishes the efficiency of the column, it is often possible to improve the results by flooding the column prior to the collection of any fractions. In cases where the entire contents of the flask need not be distilled, a better fractionation may be obtained by heating with a resistance coil, platinum or tungsten, immersed in the liquid.

Experiment 5. *Drying or Esterifying with a Fractionating Column.* (Sec. 21, 64.)—Water can be removed from liquids, solids, or reaction mixtures by means of a constant-boiling mixture, a fractionating column, and a separator. Attach a 2-l. flask (one having either two necks or a stopper large enough for two openings) containing 1 l. of 95 per cent alcohol and 200 ml. of benzene to the bottom of the fractionating column. Use a separator (the Doran type, shown in Fig. 37, or one by Hultman, Davis, and Clarke) as the receiver, and to its upper return arm connect glass tubing leading through the second opening in the distilling flask or into the fractionating column. Begin distillation. The constant-boiling mixture of alcohol, water, and benzene (Sec. 21) which comes over at 64.9° separates into two layers in the separator. The upper benzene-alcohol-rich layer returns to the distillation flask as soon as the distillate reaches the upper side arm. The lower water-rich layer is drawn off through the stopcock as desired. When two layers no longer separate in the receiver, open the cock in the bottom of the separator and let the condensate pass into a flask until all of the benzene has been removed. The temperature should then have risen to the boiling point of dry alcohol; the distillation can be stopped; and the dried residue removed.

A similar process can be applied to drying of solid. A sugar, for example, can be dissolved in alcohol, the requisite amount of benzene added, and the mixture distilled until water is removed (see Sec. 21). The anhydrous product is recovered by evaporation of alcohol. Where solid phases are present, oil- or water-bath heat should replace a free flame, or adequate stirring be provided to prevent caking and to insure intimate contact. The equilibrium in the synthesis of esters is shifted toward completion of the reaction by the removal of water as one of the volatile components (see Sec. 64).

Experiment 6. Vacuum Distillation. (Chap. 5.)—A permanent assembly consists of a manometer with a constriction in the mercury line to prevent breakage from sudden release of vacuum, a rotary oil pump protected by a cold trap as the source of vacuum, a manostat of the type described by McConnell (Fig. 48), and the vacuum-tube assembly of Huntress and Hershberg (Fig. 47) for intermittent pump operation. Select a flask with a wide (at least 12 mm. inside diameter) side arm, and attach a condenser and rotating receiver (Fig. 51) or use a flask with multiple side arms as suggested by Flosdorf and Palmer (Fig. 55). Insert the thermometer. Make sure that all joints (ground-glass or rubber stoppers are preferred) are tight. Soften any cork stoppers by rolling and bore the necessary holes with a freshly sharpened cork borer. Burning the outside of the cork is a further help in making a tight fit. Grease the stopper or ground joint, on which the rotating receiver turns, with any good commercial grease. Glycerol is frequently used as a lubricant with rubber stoppers. Fill the cold trap with freezing mixture. Test the assembly for leaks and proper pump operation before introducing the sample. Leave the stopcock of the manostat open until the desired vacuum is approached. Some allowance must be made for a lag in the movement of the mercury in the manometer. On closing the cock, the mercury should rise in the left side, make contact, and shut off the pump. Adjust the pressure by opening and closing the cock or by bleeding in air through a T tube, if necessary, until it is exactly at the point desired. The pump should then remain shut off except for infrequent operation made necessary by minor leaks. When satisfied that the system is tight and that the rotating receiver

turns easily, clamp the pressure tubing connecting permanent assembly with flask and disconnect the latter. Under no circumstances release the vacuum on the whole system without first opening the stopcock of the manostat. Add the sample furnished by the instructor for distillation, pack in enough glass wool to rise above the level of the material when liquid, and replace the flask in the system. Release the clamp gradually so as to avoid any violent movement of mercury in the manostat as well as to prevent excessive foaming of a liquid sample from escape of dissolved gases or low-boiling material. If the sample is very viscous, and foaming is troublesome, warm the flask with a beaker of hot water during this step. As soon as the vacuum is fully adjusted again, begin distillation, using an oil or metal bath as the source of heat. When distillation is completed, open the cock of the manostat before releasing the vacuum. Prompt cleaning of the apparatus after distillation saves much time. Resinous residues will usually be removed easily by adding kerosene and refluxing for a brief time.

If the assembly consisting of a mercury-vapor pump backed by a water pump (see Sec. 98), the McConnell manostat, and flutter valve is used, the operation is modified as follows: Start the water pump, and as soon as the pressure has fallen its maximum amount light the burner under the condensation pump. When the pressure has reached the desired level, close the stopcock in the manostat. The mercury will rise on the left side, make contact, and close the circuit which operates the valve. The same precautions, described in the preceding paragraph, of opening the cock on the manostat before releasing a vacuum should be observed. A manostat with flutter valve may also be used on the water pump alone if the latter is capable of maintaining the constant pressure desired.

Fractionation under vacuum (Sec. 102) can be accomplished by inserting a fractionating column in the assembly described above. Owing to the greater velocity of vapors through the column, flooding is more apt to occur. Hence it is sometimes advisable to heat with a free flame instead of a bath. Neither is it always practical to maintain jacket temperatures exactly the same as those of the vapors, higher levels often being necessary. Use oleic acid in lieu of other material.

Experiment 7. *Vacuum Distillation of Very Small Quantities.* (Sec. 72, Chap. V.)—For vacuum distillation of 0.5 ml. of material, use the method of Peakes. The flask is made from 8 cm. of 10-mm. tubing with a 1-ml. bulb. The side arm is approximately 3 cm. from the top. Condenser (6 cm. long) and two-legged rotating receiver are constructed from 5-mm. tubing. Use a thin-stem thermometer. Split a cork and wire it in place as insulation around the neck of the flask adjacent to the thermometer bulb. There should be no pockets in the condenser line where liquid can collect, and the whole apparatus should be cleaned with acid cleaning mixture to insure proper draining. Add the sample (a mixture of triacetin and dimethylaniline) with a pledget of glass wool to prevent bumping and attach to one of the permanent vacuum assemblies described above. At the end of the distillation, seal off the material collected in each arm of the rotating receiver. Use of interchangeable ground joints simplifies assembly.

Experiment 8. *Molecular Distillations.* (Sec. 103 to 107.)—Use the mercury-condensation pump with the 1.5-cm. jet backed by an oil pump. Make sure that the protecting trap is empty at the start and cooled with freezing mixture (-72°). Test the apparatus for leaks by attaching the empty flask (Hickman still, Fig. 61, or the horizontal flask, Fig. 63, for liquids; and the Washburn still, Fig. 60, for solids) to the vacuum line by means of the interchangeable ground joint. Good commercial greases are satisfactory for lubricating joints. Usually not more than 15 and never more than 30 min. is required to reach full vacuum after starting the condensation pump. Raise the mercury in the McLeod gauge and read the pressure (see Sec. 101). If a vacuum of $1\ \mu$ is not reached, test the apparatus for leaks with a standard leak detector. When the apparatus is tight, stop the pumps, release the vacuum gradually, and insert the sample (cottonseed oil, b.p. 280 to 300° , may be used) to be distilled. Repeat the exhaustion, taking care, if the sample is a liquid, lest foaming during degassing fill the flask. Warm water sometimes accelerates this step if the liquid is very viscous. The temperature of distillation is taken as that of the bath.

Experiment 9. *Superheated-steam Distillation.* (Sec. 121.)—Use the apparatus permanently set up as illustrated in Fig. 72.

Place the mixture to be distilled in the flask; insert thermometers in the vapor line and in the oil bath; and begin heating the latter. When the temperature has reached 100° or thereabouts admit steam gradually so that no solid is mechanically blown over into the receiver. If nothing distills at this temperature, begin raising both steam and bath temperatures in 25° jumps until organic matter is volatilized at an appreciable rate. Maintain it at this temperature until distillation of organic product has substantially subsided, after which apply more heat to recover any higher boiling fraction. Material stuck to the pyrex condenser wall may frequently be dislodged by draining the jacket and allowing the condenser to become hot for a short time. Use an air condenser with its end under water if sticking is very bad. At the end of the process shut off both heaters and steam and loosen all connections promptly, particularly if ground-glass joints are part of the assembly. Any residue in the flask can usually be removed by adding hot kerosene and refluxing. Under no circumstances must cleaning be delayed until after the residue has set to a hard mass. Organic material adhering to the condenser can be dislodged by attaching a flask and refluxing without circulating water through the jacket until the hot liquid has washed the condenser walls clean.

In the case of nitrated phenols the para product is obtained in very nearly pure condition. Some of the tars obtained from Friedel and Crafts or other reactions yield crystals which require further separation.

Experiment 10. *Purification by Digestion.* (See Sec. 61.)—The apparatus consists of a tube or flask of such size that a large part of the thermometer bulb is covered by the solid material being extracted, a thermometer graduated in tenths of a degree, a reflux condenser, and a water or oil bath. Place the sample in the container, insert the thermometer so that the bulb is immersed in or covered by the sample, and add solvent to cover the solid and thermometer bulb. The solvent is usually one that will dissolve impurities without appreciable quantities of the desired material. Petroleum ether or ligroin is often suitable. A mixture of solvents may be employed without affecting their utility in this experiment, as long as the composition of the mixture is not varied. Reflux the solution, using a water or oil bath as a

source of heat. After about 20 min. the temperature has reached a constant level. Usually no trouble will be experienced from superheating as long as a solid phase is present, although a little agitation with the thermometer is sometimes needed. Filter either by pouring into a Buchner funnel or by using a filter stick. Add more of the same solvent, reflux once more, and observe the temperature after equilibrium conditions have been reached. Continue the operation until the temperatures of two or more successive treatments are identical. The more soluble impurities have now been removed, and the solution contains only the pure compound or the compound with impurities that have not been entirely removed. Observe the melting point of the product after the foregoing extractions and compare with a known value for the completely purified material. The operation may be continued, if desired, until all of the product has been dissolved. A change of solvent is usually advisable if complete solution is to be attained within a reasonable time. Constancy in the boiling points of successive portions constitutes further evidence of the purity of the material, whereas a drop in the boiling point is evidence of the exhaustion of still another component. Usually the final portions of exhaustive digestion are pure materials.

Use the same apparatus to follow the progress of a reaction in which a solid phase is present, *e.g.*, conversion of a triarylcarbinol to the chloromethane compound while under a mixture of petroleum ether and acetyl chloride. All-liquid phase reactions can be similarly followed if provision is made against superheating.

Experiment 11. *Chromatographic Adsorption.* (Sec. 161 to 165.)—Use a 14-mm. tube 4 to 5 ft. long, the lower end of which is indented to hold a cotton- or glass-wool support for the adsorbent and is fitted with a rubber stopper so that it can be attached to a suction flask. Powder, not too finely, enough activated alumina to fill the tube about three-quarters full. Very fine grinding may make subsequent filtration too slow. More uniform banding can be obtained if the powder is sifted and collected between 40- to 60- or 60- to 80-mesh screens. Close the lower end of the tube and fill it about half full of ligroin or other solvent to be used and pour in the dry powder. The liquid retards settling a little, thus permitting more even packing of the adsorbent. Insert the stem of a dropping funnel well into the top of the tube and make it

fast by a section of rubber tubing which fits over both tube and stem. Pour about 100 ml. of solvent into the funnel, attach the suction flask at the bottom, and allow the filtration to begin. As the last portion of solvent leaves the funnel, pour in a solution of 0.02 g. of a mixture of anthracene and carbazole or anthracene and naphthacene dissolved in 500 ml. of petroleum ether. Use gentle suction, 680 mm., although with a graded adsorbent filtration proceeds smoothly by gravity. When the funnel is just emptying pour in 300 ml. of petroleum ether as a developing solvent. When the tube has drained, examine it for colored zones under the fluorescent light. Cut the tube so as to obtain these sections free from contamination with adjacent colored portion and elutriate by digesting the contents with alcohol-benzene mixture. Filter, allow to evaporate, and determine the melting point and weight of each fraction. The original filtrate should be examined also for unadsorbed material. Short lengths of column may be used where it is desired to adsorb impurities and recover the pure material in the filtrate.

TESTS FOR PURITY OR IDENTITY

Aside from sharp melting points, mixed melting points, microscopic examination with or without polarized light, or identity of vapor and liquid temperatures by Swietoslawski's method (Sec. 58), the methods given in the next two experiments are helpful in establishing purity or identity of compounds.

Experiment 12. *The Cooling Curve.* (See Sec. 48 to 51.)—In a Dewar test tube, of the Washburn and Read type (see Fig. 17), determine the solidification curves of naphthalene and of naphthalene with 0.2 per cent impurity, using the general method given below.

Heat the tube to approximately 100° above the melting point of naphthalene, using either a current of clean (filter air to remove grease and dust from the air line) hot air obtained by heating (with a wing-top burner) the quartz tubing which carries the air into the test tube or an internal electric heater. Remove the heater; add 0.5 g. of the melted sample (if the unmelted sample is to be added, the initial temperature must be higher); insert a thermometer, which preferably is graduated in 0.1 or 0.2° but may be only in 1° intervals; and record the temperature of the melt every 15 or

30 sec. Stir by moving the thermometer up and down. Continue observations until well below the flat portion of the curve. Plot the two curves on the same sheet of cross-section paper. Estimate the purity of the original sample and the correct melting point. Observe how near it is possible to calculate the correct melting point and molar and weight percentage impurity from the second curve alone. For compounds of higher melting point, use a liter beaker full of oil as a bath for the Dewar test tube.

Experiment 13. *Purity and Identity from the Boiling Point.* (Sec. 59 to 61.)—Use Menzies' differential thermometer and boiling-point apparatus (see Sec. 57). Add 50 mg. of asparagine and 30 ml. (the exact volume is not important unless the percentage purity is to be approximated) of reagent ethanol to the flask. Place the lighted burner so that it is directly beneath the Cottrell pump and adjust the flame so that a gentle but regular pumping, with vapors just reaching the lower end of the condenser, ensues. Violent pumping often causes erroneous results. A very fine glass spiral or loosely fitting sleeve of thin glass placed around the lower bulb of the thermometer keeps the solution in contact with the bulb for a longer time and therefore reduces fluctuations in the readings. For a similar reason the upper bulb may be wrapped with a copper-wire spiral in the manner described by Smith and Milner. Equilibrium conditions are reached in about 20 min. Read the level of the liquid in the two arms of the differential thermometer with the aid of a small lens. Turn off the burner, remove thermometer and pump, insert a filter stick, suck (water-pump vacuum) or otherwise remove the solution from the flask, add about 30 ml. of fresh solvent to the remaining solid, and repeat the operations of pumping and reading. If the temperature is the same as in the first determination, the compound is probably pure, absence of a large amount of very soluble impurity being inferred; if not the same, an impurity has been removed. Repeat the operation if necessary until two successive tests give the same result. The material is then pure as far as the presence of soluble impurities is concerned.

Another method of determining purity is to add, at the start, just enough solid to exceed the solubility in the boiling solvent and observe the temperature. Continue to add small portions of solid. The boiling point will rise with each addition if a solu-

ble impurity is present and will continue to rise until the solubility of this impurity is exceeded, that is to say, when the impurity is also present in the solid phase.

Identity of two compounds is shown in a similar manner. Add 20 mg. of glutamic acid and determine the boiling point in reagent ethanol as before. Without removing the sample add 10 mg. of asparagine and again determine the boiling temperature on the differential thermometer. Empty the apparatus, wash with ethanol, and repeat the operations reversing the order of addition. In other words, determine the boiling point in the presence of 20 mg. of asparagine and then add 10 mg. of glutamic acid. If the two substances had been identical, the boiling points in all cases would be the same. If not, there will be an elevation on the addition of the second compound. If one of the compounds being tested is very insoluble, little if any elevation will occur when added. The necessity for carrying out the test by reversing the order of addition is, therefore, obvious.

The same method can be used to measure solubility of a substance in a boiling solution provided the volume of solvent is measured and the boiling-point elevation constant is previously determined. The percentage impurity present may also be calculated, but the results are not always accurate (see Sec. 59). Identity and the presence of an impurity may be observed by direct measurement of the solubility. Indeed, the boiling-point elevation method is merely a convenient substitute for a gravimetric one.

FILTRATION AND CRYSTALLIZATION

Experiment 14.—*Filtration* with a Skau tube is often very convenient. Fill the inner tube A of a Skau filtration unit (Sec. 151) about three-quarters full of technical xylene, preferably a cut which excludes the ortho isomer. Wrap a piece of filter paper over the bottom of the porcelain filter plate, put it on top of the tube with its beveled edge toward the rim of the glass, and replace in the unit. Set the apparatus in a carbon dioxide snow freezing mixture to a depth greater than the height of liquid in the tube and allow it to remain until a substantial amount of freezing occurs. Invert the tube in a centrifuge and whirl it for a minute at about 1,400 to 1,500 r.p.m. Remove the tube and collect the

crystals of *p*-xylene which are on the filter paper. Their purity can be determined, if desired, by using a double-walled partially evacuated test tube of the Washburn type set in a freezing mixture (see Experiment 12).

p-Xylene can also be recovered by adding carbon dioxide snow gradually to 500 ml. of xylene until crystals have formed and filtering either (1) on a Buchner funnel whose bottom is covered with a bed of carbon dioxide snow or (2) with a filter stick or cloth-covered funnel inserted in the solution. In either event a mercury-condensation pump backed by a water pump is indispensable if a reasonably rapid filtration is desired. Press and otherwise work the crystals with the flattened closed end of a tube partially filled with carbon dioxide snow. *Caution!* Do not handle the cold part of the tube in the hands. Determine the purity of the resulting product by means of the cooling curve as described in the preceding paragraph.

Experiment 15. *Crystallization of Lactic Acid.* (See Sec. 134.)—The problem of crystallizing lactic acid is essentially one of freeing the material from water at a temperature low enough to prevent formation of lactide. It is done most conveniently by means of a vacuum pump of high capacity, producing a very low vacuum. Use the mercury-condensation pump backed by the oil pump and the horizontal-flask molecular still shown in Fig. 63. Place 500 ml. of lactic acid with glass-wool packing in the flask and attach a rotating receiver (Fig. 5). Connect the flask to the vacuum assembly through a cold trap whose inlet tube must be wide enough to avoid plugging from the frozen water. Start the pumps and remove the bulk of the water at room temperature. After drying for two or three hours in this way, warm the flask with a water bath until the last traces of water are removed. Continue heating until lactic acid begins to distill (bath temperature 80°). Collect the lactic acid and repeat the operation. If the optically active form of lactic acid is being distilled it will usually crystallize spontaneously during the second or third distillation. Formation to crystals is accelerated by cooling a section of the tube leading to the condenser with carbon dioxide snow. A short recessed section made by pressing in a portion of the wall with a spatula or other tool is often an adequate well for a freezing mixture.

Crystallization of Sirupy Mixtures.—In general, subject to systematic study all sirupy mixtures that are difficult to crystallize. The following suggestions are helpful: (1) Fractionally distill the sirup under vacuum in order to get a cut in which the desired product will be more concentrated. If the compound decomposes, even in a molecular still, convert it if possible into a volatile derivative which can be fractionated and then converted back into the original compound. (2) Try cooling the sirup to different temperatures while scratching the container wall with a stirring rod. Try to establish a gradient through the mass by uneven cooling. Allow to warm and cool again. Repeat several times. (3) Change the surface area by pouring some of the liquid into a test tube, warming and rotating the tube to wet the wall, draining the tube, and cooling the thin film with scratching in order to get seed crystals. As an alternative wet a glass bead with a thin film of the sirup, put in a test tube, and cool with rubbing to different temperatures. If crystals form, roll the glass bead with its crystals into the main body of the sirup cooled to the desired temperature. (4) Dissolve a few drops of the sirup in a milliliter each of different solvents such as methanol, ethanol, ethyl acetate, acetone, anhydrous ether, toluene, pentane, or carbon tetrachloride-chloroform mixture, which can be cooled to very low temperatures without solidifying. Cool to low temperatures with wall scratching to induce crystallization. If crystals fail to form within a reasonable time, let the solutions stand in the icebox for a few days. (5) Put a little of the sirup in a mortar, add petroleum ether or other poor solvent, and grind with a pestle. Continue rubbing for at least half an hour before abandoning the effort. The addition of a little carbon or silica gel is sometimes helpful in inducing crystallization by this method. (6) Soak the sirup in a vacuum oven or, better, under a mercury-condensation pump and apply gentle warming in order to vaporize traces of low-boiling substances which inhibit crystallization. (7) Spread the sirup in a thin layer on the bottom of a beaker or in a stoppered Erlenmeyer flask if it is hygroscopic. Label and set aside for an indefinite period. Colored sirups may be treated in this manner or preferably may be decolorized with carbon before standing.

If crystals form from a thick sirup at any time, whether in the pure or crude material, they should be subjected to treatment that will preserve their crystalline form. Add a small amount of solvent such as petroleum ether or cold alcohol which will wash the oil from the crystals. Keep a tiny sample for seeding and then recrystallize the remainder. The oily material obtained by washing should be distilled or otherwise concentrated in order to get more crystals.

MISCELLANEOUS EXPERIMENTS

Experiment 16. *Determination of the Number of Theoretical Plates in a Fractionating Column.* (Sec. 82.)—Arrange the distillation flask so that a sample can be removed promptly while one is being taken from the top of the column (see Fig. 35). Add 30 ml. of a mixture of 35 mol percentage of carbon tetrachloride with benzene. Operate the column under total reflux, *i.e.*, with no collection of condensate in the receiver. Allow ample time, say one hour, for attainment of equilibrium before drawing off samples for analysis. Determine the index of refraction of the samples from the top and bottom of the column and mark their position on the graph (at least 20 by 15 in. in size) of Rosanoff and Easley's data. Draw a series of vertical and horizontal lines as shown in Fig. 36 between the two points. The number of steps, less one for the still itself, which serves as a plate, is the total number of plates in the column. Find the H.E.T.P. by dividing the height of the column by the number of plates.

Experiment 17. *Reaction in an Inert Atmosphere.*—Construct an apparatus of the type used by Ziegler (see Fig. 122). Add 0.1 g. of triphenylchloromethane to 0.5 g. of dried molecular silver in one arm. In the other arm put anhydrous ether. Set the part of the apparatus containing ether in a freezing mixture, attach a water vacuum, and exhaust. Release the vacuum, meanwhile admitting carbon dioxide. Exhaust again and repeat the operation once more. On the final exhaustion, seal the apparatus, using a flame that is not too pointed. It is sometimes advisable, in the construction of the apparatus, to thicken or narrow the place that is to be sealed so that the tube is not blown inward during this operation. When the seal has cooled, distill

the ether on to the solid materials by cooling the latter. When the reaction has taken place, filter the solution into the other compartment. Distill some of the ether back into the reaction arm as a washing liquid. Concentrate the solution of the free radical until crystals form. Filter the mother liquor into the other compartment, free the crystals from the remainder of the solvent by warming them in a water bath while cooling the other side and seal off the tube containing the crystals of triphenylmethyl.

The same apparatus can be used with any reaction that requires an inert atmosphere.

Experiment 18. *Macro Experiments.*—In preparation of large quantities of any material, irrespective of the description supplied in the literature for working up the product, pay attention to the following points:

1. Substitution of inverted-siphon filters for the conventional type when handling large quantities of solution.
2. Systematic digestion or extraction of solid products before any attempt at crystallization is made.
3. Thorough removal of all volatile matter from oily or noncrystalline materials by steam distillation, superheated-steam distillation, digestion, or prolonged application of a very low vacuum.
4. Continuous-extraction apparatus, *e.g.*, a percolator which will accomplish in many cases a result similar to that obtained by exhaustive digestion accompanied, whenever possible, by boiling-point measurements to show the progress of purification.
5. Use of an automatic separator of the type employed by Hultman, Davis, and Clarke in place of the cumbersome large separatory funnels when large quantities of solution must be handled.
6. Under no circumstances throw away a tarry product without first subjecting it to superheated-steam, codistillation with petroleum, or vacuum distillation.

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